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Organocatalyst-assisted Ar-^{18}F bond formation: A universal procedure for direct aromatic radiofluorination

Jimmy Erik Jakobsson, Gaute Grønnevik and Patrick Johannes Riss*[a,b]

Contents

1. Materials, Methods and Experiments

Reactants, reagents and solvents used herein were procured from Sigma-Aldrich (Sigma-Aldrich AS, Norway) in analytical quality unless specified otherwise. Solid phase extraction (SPE) cartridges were purchased from VWR (VWR International, Darmstadt, Germany). Nuclear magnetic resonance spectra were recorded on a Bruker AVII 400 NMR instrument (Bruker ASX Nordic AB). Chemical shifts (δ) for proton (400 MHz) and ^{13}C (100 MHz) resonances are reported in parts per million (ppm), relative to the solvent signal ($CDCl_3$ δ = 7.226 ppm), downfield from the expected tetramethylsilane signal (TMS, δ = 0 ppm). Mass spectrometry was conducted on a Q-Tof-2 mass analyser (Micromass, Q-Tof-2™) using electron spray ionization in positive mode (+ESI). For quality control and analysis of the radiochemical yield, a Phenomenex Luna PFP(2) column (5 µm, 100 Å, 250 mm × 4.6 mm) or a Supelco HS F5 of equal dimensions were used as a stationary phase with an isocratic mixture of MeCN-water as a mobile phase at a flow rate of 1.5 ml/min. RadioTLC was conducted on Silica gel 60 F_{254} coated aluminum TLC plates (Supelco, USA). RadioTLC plates were analysed using a raytest miniGita radioTLC scanner (Raytest GmBH, Straubenhardt, Germany). All other radioactivity measurements during labelling experiments and radiotracer productions were performed using a Wallac Wizard well counter (PerkinElmer, Oslo, Norway).

2. Initial radiochemistry – literature procedure:

We chose a reproduction of literature results for radiofluorination of known iodane precursors as a starting point for our investigation. Besides published procedures, we explored a number of standardised labelling protocols of common use in the PET chemistry community. Table S1 illustrates the outcome of baseline experiments.

Table S1: Yields for baseline experiments in comparison to literature and screening results.

Entry (substrate)	Conditions	Product	RCY / %[a]	
			Lit.	Lab.
1 (**1**)	DMF, crypt-222, K_2CO_3 130 °C, 20 min	4-[^{18}F]fluorophen-1-yl benzyl ether	25±5[a]	45±11
2 (**2**)	DMF, crypt-222, K_2CO_3 130 °C, 20 min	4-[^{18}F]fluoroanisol	15 ±5[a]	11±1
3 (**1**)	DMF/DMSO, crypt-222, K_2CO_3 130 °C, 20 min	4-[^{18}F]fluorophen-1-yl benzyl ether		33.5(1)
4 (**1**)	DMF, crypt-222, KH_2PO_4	4-[^{18}F]fluorophen-1-yl		9.6 (1)

	130 °C, 20 min	benzyl ether		
5 (**1**)	DMF, crypt-222, KH_2PO_4/ K_2CO_3 1:1 130 °C, 20 min	4-[^{18}F]fluorophen-1-yl benzyl ether		35.2 (1)
6 (**1**)	DMF, crypt-222, KH_2PO_4/ K_2CO_3 9:1 130 °C, 20 min	4-[^{18}F]fluorophen-1-yl benzyl ether		35.7 (1)
7 (**1**)	DMF, crypt-222, K_2CO_3 130 °C, 20 min	N-(4-[^{18}F]fluoro phen-1-yl-N-methylformamide	n.a.	91±3
8 (**1**)	MeCN, crypt-222, K_2CO_3 130 °C, 20 min	4-[^{18}F]fluorophen-1-yl benzyl ether	31[b]	
9 (**2**)	MeCN, crypt-222, K_2CO_3 130 °C, 20 min	4-[^{18}F]fluoroanisol	16[b]	

A = Rotstein et. al. Triethylammonium bicarbonate, DMF
B = Cardinale crypt-222/K_2CO_3, MeCN or DMF

As expected and consistent with literature reports, electron rich, i.e. strongly deactivated S_NAr substrates were labelled, albeit to a low extend (table 1, entry 1-2) insufficient for routine application. Moreover, yields for substrate **1** are very variable when replicated. For us this observation was very meaningful since aromatic substitutions under no-carrier-added (n.c.a) conditions are normally quite robust. Despite good efforts including model reactions using activated nitro-precursors for benchmarking of RCY, basic tweaking of the described conditions did not lead to an improvement. We, hence, hypothesised that the yield was affected by a poorly controlled yet unknown reaction condition.
In initial experiments with the aim to analyse fluorination reactions based on iodanes, we observed PhIO as a side product when excess base was present in the reaction mixture, therefore we experimented with milder bases to see if this might help stabilising the outcome, however, no useful improvement was observed (table 1, entry 3-6). Variation of the solvent (entry 3) was equally fruitless. Entries 8 and 9 show published results from an earlier study in MeCN. When attempting a reproduction we struggled with partial evaporation of the solvent and discarded the tests. Nonetheless, we were able to match literature yields within the first few attempts by simply following the published procedures. Such basic reproducibility gave us confidence in the following optimisation study.

3. Quality control, determination of radiochemical yield and identity of labelled products:

Quality control of final radiotracers and labelled model compounds was conducted using a radioHPLC system. Radiochemical yields were primarily determined using radioTLC and radioHPLC unless volatile products were present. In these cases, yields were determined by radioHPLC alone.

Identity of labelled products was determined by coinjection of a non-radioactive reference compound. The delay between the serially connected UV and radioactivity detectors was measured so that identity of products could be confirmed by co-elution of sample and reference, respectively.

3.1 RadioHPLC analysis:

An aliquot of the reaction mixture (20 µl) was withdrawn and diluted with HPLC mobile phase (200 µl) and 5-20 µl of the diluted sample were injected manually into the HPLC system. The mobile phase used for all HPLC experiments was MeCN-H_2O, 1:1 at a flowrate of 1.5 ml/min. A Phenomenex Luna PFP(2) pentafluorophenyl modified silica gel column, particle size 5 µm, pore size 100 Å of the dimensions 250 mm x 4.6 mm was used as stationary phase.

3.2 RadioTLC analysis:

An aliquot of the reaction mixture (10 µl) was withdrawn and diluted with CH_2Cl_2 (30 µl). TLC samples were spotted 10 mm from the bottom end of 67 mm long TLC plates and briefly dried at RT. Plates were were developed in saturated glass chambers using the mobile phases shown in Table S2 until solvent reached the top end. The TLC plates were analysed using a raytest miniGITA radioHPLC detector in scanning mode over the distance of 0-70 mm from the bottom end of the plate for 1 minute.

3.3 Chemical purity:

Chemical purity was determined after substraction of background. The percentage of pure product was obtained from the peak area of the HPLC UV signal in the product region in chromatograms followed by division of the area obtained for the integral of the entire HPLC-UV-trace. The obtained fraction was multiplied by 100%:

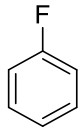
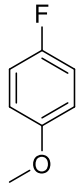
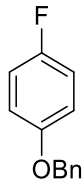
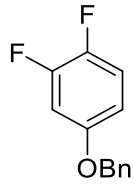
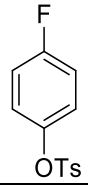
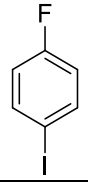
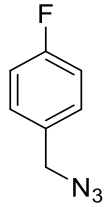
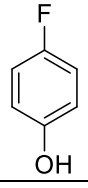
$$Purity = \frac{Signal\ area\ (Product)}{Signal\ area\ (Total\ chromatogram)} \times 100\%$$

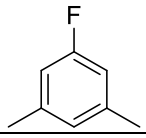
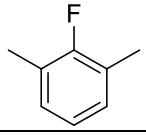
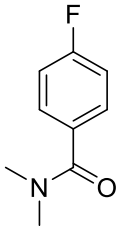
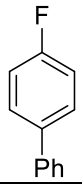
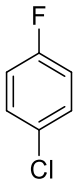
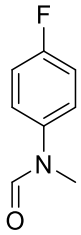
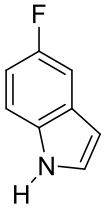
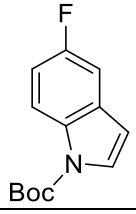
3.4 Molar radioactivity:

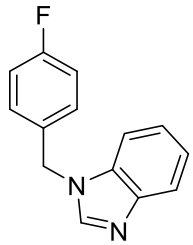
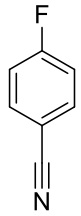
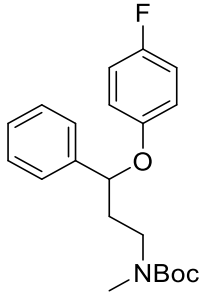
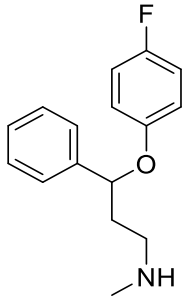
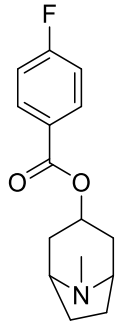
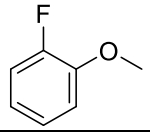
A dose calibrator and UV-HPLC were used for determination of the molar radioactivity A_M. The activity of the product A_V (in 1 mL) was measured using a calibrated ionisation chamber. Linearity of the UV response in the relevant concentration range (0.1-10 nmol/mL) was confirmed by injection of serial dilutions of the reference compound. Peak areas Area(Reference) obtained were plotted against reference concentration c(Reference) of each individual sample to allow for linear regression analysis. To determine concentration of the product, the peak area of the product was divided by the peak area of a known reference within the linear range and multiplied by the reference concentration:

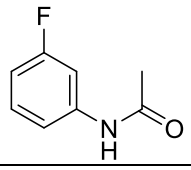
$$c(Product) = \frac{Area\ (Product)}{Area\ (Reference)} \times c(Reference); \quad A_M = \frac{A_V\ (Product)}{c(Product)};\ [A_M] = \frac{Bq}{mol}$$

Table S2: TLC retention factors and HPLC retention time for key radiolabelled compounds.

Entry	***Product***	***TLC retention factor***	***HPLC retention time***
1		***NA***	***07:12***
2		***NA***	***07:31***
3		***0.50[a]***	***19:56***
4		***0.50[b]***	***21:12***
5		***NA***	***18:55***
6		***NA***	***11:58***
7		***0.52[a]***	***09:35***
8		***NA***	***03:43***

9		***NA***	***14:40***
10		***NA***	***14:09***
11		***0.74[c]***	***02:55***
12		***0.38[b]***	***20:25***
13		***NA***	***----------***
14		***0.45[d]***	***05.11[e]***
15		***0.58[f]***	***07:14***
16		***0.65[f]***	***NA***

17		***NA***	***5:31***
18		***NA***	***05:23***
19		***0.48[g]***	***17:31[h]***
20		***NA***	***2:58[h]***
21		***0.38[i]***	***NA***
22		***NA***	***06.55***

23		***0.60[c]***	***03.23***

1: RadioTLC conditions: a = EtOAc-hexane, *3:40*; *b)* = Hexane*;* c) = MeOH-CH_2Cl_2, *1:24* d) = MeOH-CH_2Cl_2, *1:49* e) = MeCN-MOPS (0.05M, pH 7.4), *4:6*; f) = EtOAc-hexane, *1:1*; g) = EtOAc-hexane: *1:4*; h) = H_2O-MeCN, *9:11*; i) = MeOH-$CHCl_3$, 1:9 (0.7% NH_4OH)

2: RadioHPLC conditions: Flow rate: 1.5 ml/min; Column: Luna PFP(2); Mobile phase: MeCN-H_2O: 1:1

4. Synthesis of starting materials, reference compounds and labelled products

4.1 Typical procedure A (ylide synthesis)[i].

Reaction mixtures were kept in the dark at all times. In a glass vial 3-chloroperbenzoic acid (77%, 1.4 mmol, 310 mg) was dissolved in DCM (5 ml) and left for 5 minutes (excess water adhered to glass walls of vial). To iodoarene (1 mmol) in a capped argon flushed vial was added the 3-chloroperbenzoic acid solution, care was taken to avoid transferring water droplets. The reaction mixture was heated to 39 degrees for 80 minutes. Major to full consumption of starting material was indicated via TLC analysis (8% MeOH in DCM), (under UV light was all intermediate compounds visible in red that upon iodine staining yielded cream white coloured crescents. The reaction mixture was cooled to 10-15 ^{o}C. In one portion was added KOH (10 mmol, 560 mg) and 2,2-dimethyl-1,3-dioxane-4,6-dione (1.3 mmol, 187 mg). The reaction mixture was kept for 10– 60 minutes until complete conversion of intermediate was observed via TLC analysis (8% MeOH in DCM) (new in UV light visible bands that upon iodine staining stain in cream white, typically R_f is similar to intermediate). The reaction mixture was diluted with DCM (10 ml), filtered through a filter paper, washed with DCM (10 ml) and dried over sodium sulfate. The drying agent was filtered off and solvent removed under reduced pressure at 20-22 ^{o}C. The crude solids were dissolved in a minimal amount of DCM and filtered through a filter paper. The compounds were purified via precipitation from addition of hexanes (20 ml). The flasks were left at -20 for 1 hour. The pure ylides were obtained via decanting the solvents and solids washed with hexanes.

4.2 Typical procedure B (ylide synthesis)

To λ^3-iodane diacetate (1 mmol) in DCM (5 ml) at 10-15 ^{o}C was added in one portion KOH (10 mmol, 560 mg) and 2,2-dimethyl-1,3-dioxane-4,6-dione (1.3 mmol, 187 mg) and the reaction mixture kept for 10 min – 60 minutes until complete conversion of intermediate was observed via TLC analysis (8% MeOH in DCM) (new in UV light visible bands that upon iodine staining stain in cream white, typically Rf is very similar to intermediate). The reaction mixture was diluted with DCM (10 ml), filtered through cotton and glass wool, washed with DCM (10 ml) and dried over sodium sulfate. The drying agent was filtered off and the solvent removed in an aluminium foil wrapped round bottom flask under reduced pressure at 22 ^{o}C. The crude solids were purified via precipitation from dissolving in DCM (10 ml) and adding hexanes (20 ml). The flasks were left at -20 for 1 hour. The pure ylides were obtained via decanting the solvents and washed with hexanes.

4.3 Removal of iodine

We observed a brownish discolouration of the reaction mixture in several experiments. A mildly redish colour evident in labeling precursors coincided with lower labeling yield. We surmised iodine formation as the origin of the colour and decided to investigate reduction

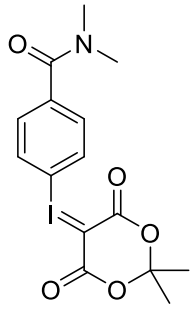
of the iodine by a sulfite wash. Indeed, labeling yields improved drastically when adding an aqueous workup with dilute sulfite solution.

4.4 Radiolabelling

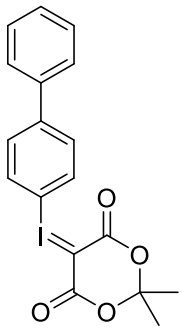
Aqueous target mixtures containing $^{18}F^-$ (50-300 MBq) was loaded onto a QMA cartridge and subsequently eluted with K222 (40 mg, 106 µmol) and K_2CO_3 (7.36 mg, 44.4 µmol) in 30/70 water/acetonitrile (1 ml) into a V-vial. The vial was heated at 85°C under a stream of nitrogen. After evaporation of bulk solvents, AcN (1 ml) was added. The process was repeated 2 consecutive times. The vials content was equally distributed into 4 V-vials from DMF (1000 µl).

To each V-vial was added iodonium ylide (10 µmol) and additive from DMF (0.75 ml). The capped V-vial was either bubbled with nitrogen for 1 minute or directly heated in a heating block at 130 °C for 20 minutes. The reaction mixture was allowed to cool to room temperature and a sample was taken for TLC and/or HPLC analysis.

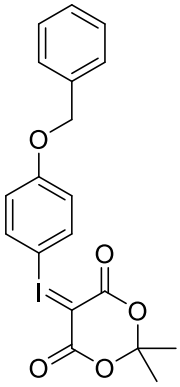
5. Analytical data and procedures



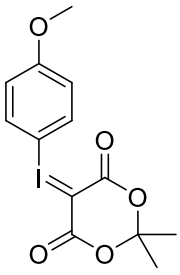
Synthesised according to typical procedure A. 4-((2,2-dimethyl-4,6-dioxo-1,3-dioxan-5-ylidene)-l3-iodaneyl)-N,N-dimethylbenzamide. Reaction performed on 0.5 mmol scale yielding target compound in 14% yield (60 mg, 0.14 mmol) as white solids.^{1}H NMR (400 MHz, DMSO-d_6) δ 7.86 – 7.80 (m, 1H), 7.51 – 7.44 (m, 1H), 2.98 (s, 2H), 2.86 (s, 2H), 1.58 (s, 3H). ^{13}C NMR (101 MHz, DMSO) δ 168.7, 162.9, 138.7, 132.3, 129.3, 116.7, 102.8, 57.8, 38.9, 34.7, 25.6. HR-ESIMS: *m/z* 439.9966 $[M+Na]^+$ ($C_{15}H_{16}INNaO_5^+$, calculated 439.9965)



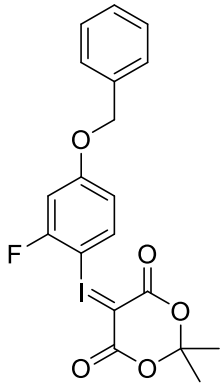
Synthesised according to typical procedure A. 5-([1,1'-biphenyl]-4-yl-l3-iodaneylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione. Reaction performed on 1 mmol scale yielding target compound in 49% yield (206 mg, 0.49 mmol) as beige solids. Analytical data was in accordance to that previously reported[ii]. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.89 – 7.83 (m, 2H), 7.78 – 7.72 (m, 2H), 7.71 – 7.65 (m, 2H), 7.49 (dd, *J* = 8.3, 6.7 Hz, 2H), 7.45 – 7.38 (m, 1H), 1.58 (s, 6H). ^{13}C NMR (101 MHz, DMSO) δ 162.9, 142.5, 138.5, 133.1, 129.1, 129.1, 128.3, 126.9, 115.0, 102.7, 57.9, 25.6. HR-ESIMS: *m/z* 444.9907 $[M+Na]^+$ ($C_{18}H_{15}INaO_4^+$, calculated 444.9907)



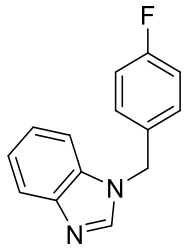
Synthesised according to typical procedure A. 5-((4-(benzyloxy)phenyl)-l3-iodaneylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione. Reaction performed on 1 mmol scale yielding target compound in 43% yield (196 mg, 0.43 mmol) as white solids. Analytical data was in accordance to that previously reported.[iii] ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.76 – 7.65 (m, 2H), 7.50 – 7.27 (m, 5H), 7.14 – 7.05 (m, 2H), 5.14 (s, 2H), 1.54 (s, 6H). ^{13}C NMR (101 MHz, DMSO) δ 162.8, 160.1, 136.3, 134.6, 128.5, 128.0, 127.8, 117.4, 106.0, 102.6, 69.5, 58.5, 25.6. HR-ESIMS: *m/z* 475.0012 $[M+Na]^+$ ($C_{19}H_{17}INaO_5^+$, calculated 475.0012)



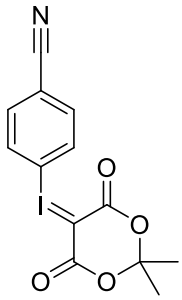
Synthesised according to typical procedure A. 5-((4-methoxyphenyl)-l3-iodaneylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione. Reaction performed on 1 mmol scale yielding target compound in 54% yield (203 mg, 0.54 mmol) as white solids. Analytical data was in accordance to that previously reported[iv]. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.74 – 7.68 (m, 2H), 7.04 – 6.98 (m, 2H), 3.78 (s, 3H), 1.54 (s, 6H). ^{13}C NMR (101 MHz, DMSO) δ 162.8, 161.1, 134.7, 116.6, 105.8, 102.6, 58.5, 55.5, 25.6. **HR-ESIMS:** *m/z* 398.9700 $[M+Na]^+$ ($C_{13}H_{13}INaO_5^+$, calculated 398.9700)



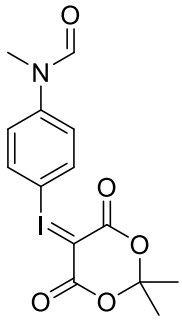
Synthesised according to typical procedure A. 5-((4-(benzyloxy)-2-fluorophenyl)-l3-iodaneylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione. Reaction performed on 1 mmol scale yielding target compound in 41% yield (192 mg, 0.41 mmol) as beige solids. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.81 (dd, J = 8.8, 7.0 Hz, 1H), 7.59 – 7.30 (m, 5H), 7.15 (dd, J = 10.4, 2.7 Hz, 1H), 6.94 (dd, J = 8.9, 2.7 Hz, 1H), 5.17 (s, 2H), 1.50 (s, 6H). ^{19}F NMR (377 MHz, DMSO) δ -96.5. ^{13}C NMR (101 MHz, DMSO) δ 162.6, 162.4 (d, $^{3}J_{CF}$ = 11 Hz), 160.5 (d, $^{1}J_{CF}$ = 248 Hz), 136.9 (d, $^{4}J_{CF}$ = 4 Hz), 135.9, 128.5, 128.2, 127.9, 113.8 (d, $^{3}J_{CF}$ = 3 Hz), 103.0 (d, $2J_{CF}$ = 26 Hz),102.5, 93.8 (d, $2J_{CF}$ = 26 Hz), 70.1, 59.3, 25.5. HR-ESIMS: *m/z* 492.9919 $[M+Na]^+$ ($C_{19}H_{16}FINaO_5^+$, calculated 492.9919)



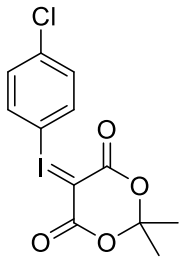
Synthesised according to typical procedure B. 2,2-dimethyl-5-(phenyl-l3-iodaneylidene)-1,3-dioxane-4,6-dione. Reaction performed on 1 mmol scale yielding target compound in 60% yield (206 mg, 0.6 mmol) as white solids. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.83 – 7.75 (m, 2H), 7.60 – 7.51 (m, 1H), 7.46 (dd, J = 8.4, 7.0 Hz, 2H), 1.56 (s, 6H). ^{13}C NMR (101 MHz, DMSO) δ 162.8, 132.5, 131.0, 130.6, 116.3, 102.7, 57.8, 25.6. Analytical data was in accordance to that previously reported[v]. HR-ESIMS: *m/z* 368.9595 $[M+Na]^+$ ($C_{12}H_{11}INaO_4^+$, calculated 368.9594)



Synthesised according to typical procedure A. 4-((2,2-dimethyl-4,6-dioxo-1,3-dioxan-5-ylidene)-l3-iodaneyl)benzonitrile. Reaction performed on 1 mmol scale yielding target compound in 21% yield (77 mg, 0.21 mmol) as white solids. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.91 – 7.82 (m, 4H), 1.51 (s, 6H). ^{13}C NMR (101 MHz, DMSO) δ 162.9, 134.3, 132.9, 121.3, 117.7, 113.4, 103.0, 58.2, 25.6. **HR-ESIMS:** *m/z* 393.9546 $[M+Na]^+$ ($C_{13}H_{10}INNaO_4^+$, calculated 393.9547)

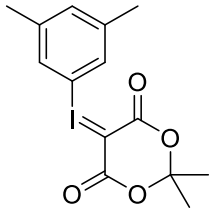


Synthesised according to typical procedure A. N-(4-((2,2-dimethyl-4,6-dioxo-1,3-dioxan-5-ylidene)-l3-iodaneyl)phenyl)-N-methylformamide. Reaction performed on 1 mmol scale yielding target compound in 22% yield (89 mg, 0.22 mmol) as beige-grey solids. Recoding NMR spectra yielded a mixture of rotary isomers in 1:8. ^{1}H NMR (400 MHz, DMSO-d_6) δ (8.65, 8.40) (s, 1H), (7.65 – 7.61, 7.85 – 7.75 (m, 2H)), 7.66 – 7.38 (m, 2H), (3.32, 3.21 (s, 3H)), 1.56 (s, 6H). ^{13}C NMR (101 MHz, DMSO) δ 162.9, 162.1, 144.1, 133.8, 122.9, 111.4, 102.7, 58.3, 30.5, 25.6. HR-ESIMS: *m/z* 425.9810 $[M+Na]^+$ ($C_{14}H_{14}INNaO_5^+$, calculated 425.9809)

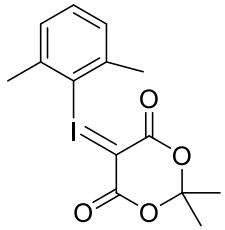


Synthesised according to typical procedure A 5-((4-chlorophenyl)-l3-iodaneylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione. Reaction performed on 2 mmol scale yielding target

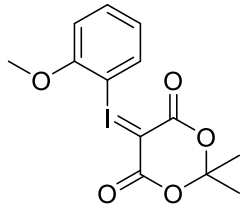
compound in 25% yield (194 mg, 0.50 mmol) as white solids. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.82 – 7.76 (m, 2H), 7.58 – 7.52 (m, 2H), 1.57 (s, 6H). ^{13}C NMR (101 MHz, DMSO) δ 162.8, 135.8, 134.2, 130.9, 114.2, 102.8, 58.3, 25.6. HR-ESIMS: *m/z* 402.9205[M+Na]$^{+}$ ($C_{12}H_{10}ClINaO_4^{+}$, calculated 402.9204)



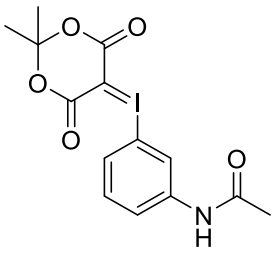
Synthesised according to typical procedure A 5-((3,5-dimethylphenyl)-l3-iodaneylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione. Reaction performed on 2 mmol scale yielding target compound in 41% yield (310 mg, 0.83 mmol) as white solids. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.44 – 7.39 (m, 2H), 7.19 (dt, *J* = 1.7, 0.9 Hz, 1H), 2.29 (s, 6H), 1.56 (s, 6H). ^{13}C NMR (101 MHz, DMSO) δ 162.8, 140.4, 132.2, 129.9, 116.3, 102.6, 57.7, 25.6, 20.7. HR-ESIMS: *m/z* 396.9907[M+Na]$^{+}$ ($C_{14}H_{15}INaO_4^{+}$, calculated 396.9907)



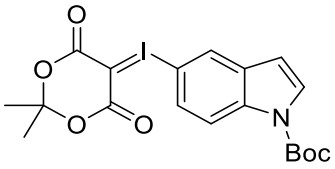
Synthesised according to typical procedure A 5-((2,6-dimethylphenyl)-l3-iodaneylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione. Reaction performed on 1.4 mmol scale yielding target compound in 34% yield (180 mg, 0.48 mmol) as white solids. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.35 (dd, *J* = 8.0, 6.8 Hz, 1H), 7.24 (d, *J* = 7.4 Hz, 2H), 2.68 (s, 6H), 1.46 (s, 6H). ^{13}C NMR (101 MHz, DMSO) δ 162.6, 141.5, 131.4, 127.9, 126.6, 102.4, 56.7, 26.5, 25.5. HR-ESIMS: *m/z* 396.9908[M+Na]$^{+}$ ($C_{14}H_{15}INaO_4^{+}$, calculated 396.9907)



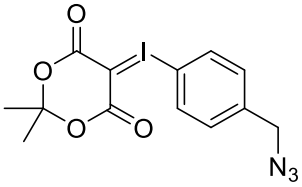
Synthesised according to typical procedure A. 5-((2-methoxyphenyl)-l3-iodaneylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione. Reaction performed on 2 mmol scale yielding target compound in 50% yield (379 mg, 1.01 mmol) as white solids. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.47 (ddd, *J* = 8.4, 7.4, 1.5 Hz, 1H), 7.35 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.09 (ddd, *J* = 8.4, 7.4, 1.3 Hz, 1H), 6.97 (dd, *J* = 8.2, 1.2 Hz, 1H), 3.97 (s, 3H), 1.79 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.75, 155.29, 132.85, 128.82, 124.62, 112.48, 104.82, 101.81, 57.12, 47.56, 26.16. HR-ESIMS: *m/z* 398.9700 [M+Na]$^{+}$ ($C_{13}H_{13}INaO_5^{+}$, calculated 398.9700)



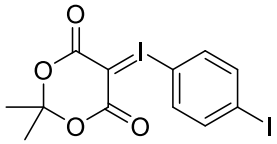
N-(3-((2,2-dimethyl-4,6-dioxo-1,3-dioxan-5-ylidene)-l3-iodaneyl)phenyl)acetamide. Synthesised via **(3-acetamidophenyl)-l3-iodanediyl diacetate** and ylide formation step was performed in accordance to [ii]. The target compound was obtained as white solids in 5% (23 mg 0.06 mmol). ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.24 (s, 1H), 8.11 (t, J = 1.9 Hz, 1H), 7.71 – 7.64 (m, 1H), 7.47 – 7.42 (m, 1H), 7.35 (t, J = 8.0 Hz, 1H), 2.05 (s, 3H), 1.56 (s, 6H). ^{13}C NMR (151 MHz, DMSO) δ 168.7, 162.8, 140.9, 131.0, 127.0, 122.4, 120.8, 116.3, 102.7, 57.9, 25.6, 24.0. HR-ESIMS: *m/z* 425.9810 $[M+Na]^+$ ($C_{14}H_{14}INNaO_5^+$, calculated 425.9809)



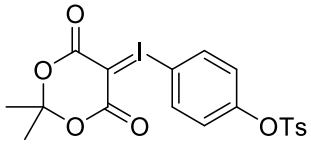
Synthesised according to typical procedure A tert-butyl 5-((2,2-dimethyl-4,6-dioxo-1,3-dioxan-5-ylidene)-l3-iodaneyl)-1H-indole-1-carboxylate. Reaction performed on 2 mmol scale yielding target compound in 18% yield (170 mg, 0.35 mmol) as white solids. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.17 – 8.04 (m, 1H), 7.84 – 7.69 (m, 1H), 1.63 (s, 4H), 1.54 (s, 3H). ^{13}C NMR (101 MHz, DMSO) δ 162.8, 148.6, 135.2, 131.9, 128.2, 128.0, 126.3, 117.0, 109.7, 107.1, 102.6, 84.7, 58.6, 27.6, 25.6. HR-ESIMS: *m/z* 508.0228$[M+Na]^+$ ($C_{19}H_{10}INNaO_6^+$, calculated 508.0228)



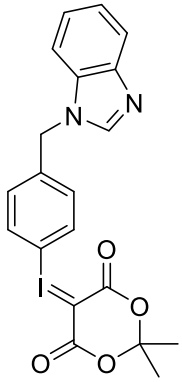
Synthesised according to typical procedure A 5-((4-(azidomethyl)phenyl)-l3-iodaneylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione Reaction performed on 2 mmol scale yielding target compound in 34% yield (270 mg, 0.67 mmol) as pale yellow solids. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.85 – 7.78 (m, 2H), 7.48 – 7.40 (m, 2H), 4.52 (s, 2H), 1.56 (s, 6H). ^{13}C NMR (101 MHz, DMSO) δ 162.8, 138.6, 132.9, 130.7, 115.7, 102.7, 58.1, 52.7, 25.6. HR-ESIMS: *m/z* 423.9765$[M+Na]^+$ ($C_{13}H_{12}IN_3NaO_4^+$, calculated 423.9765)



5-((4-iodophenyl)-l3-iodaneylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione dione Reaction performed on 4 mmol scale yielding target compound in 28% yield (523 mg, 1.1 mmol) as white solids. Analytical data was in accordance to that previously reported. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.86 – 7.79 (m, 2H), 7.58 – 7.50 (m, 2H), 1.56 (s, 6H). ^{13}C NMR (101 MHz, DMSO) δ 162.8, 139.6, 134.3, 115.8, 102.8, 98.1, 58.1, 25.6. HR-ESIMS: *m/z* 494.8561 $[M+Na]^+$ ($C_{12}H_{10}I_2NaO_4^+$, calculated 494.8561)

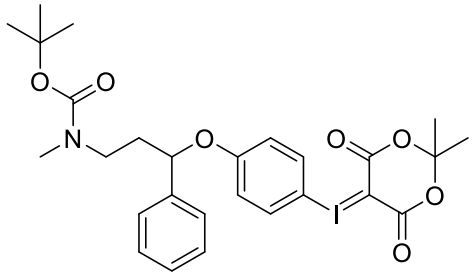


4-((2,2-dimethyl-4,6-dioxo-1,3-dioxan-5-ylidene)-l3-iodaneyl)phenyl 4-methylbenzenesulfonate. Sodium hydroxide (264 mg, 6.6 mmol) was dissolved in acetic acid (5 ml) and acetic anhydride (1 ml). sodium periodate (674 mg, 3.2 mmol) and 4-iodophenyl 4-methylbenzenesulfonate (1120 mg, 3 mmol) was added. The reaction mixture was heated to 115 degrees for 3 hours. The reaction mixture was diluted with water and extracted with DCM. The combined organic phases were washed with sodium hydrogen carbonate and dried over sodium sulfate. Diethyl ether (50 ml) was added and the mixture sonicated. The solids were filtered off and rinsed with diethyl ether (15 ml * 2). The obtained white solids were used in the next step without further purification.
To above was 0.5 mmol used for ylide formation via general procedure B on 0.5 mmol scale yielding target compound in 45% (116 mg, 0.23 mmol) as white solids. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.82 – 7.71 (m, 4H), 7.48 (d, J = 8.1 Hz, 2H), 7.18 – 7.10 (m, 2H), 2.42 (s, 3H), 1.55 (s, 6H). ^{13}C NMR (101 MHz, DMSO) δ 162.8, 150.4, 146.1, 134.3, 131.0, 130.4, 128.2, 124.7, 114.1, 102.8, 58.3, 25.5, 21.2. HR-ESIMS: *m/z* 538.9632 $[M+Na]^+$ ($C_{19}H_{17}INaO_7S^+$, calculated 538.9632)

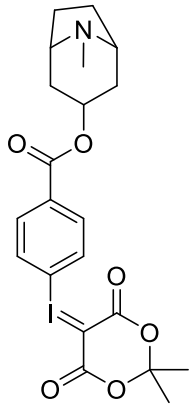


1-(4-((2,2-dimethyl-4,6-dioxo-1,3-dioxan-5-ylidene)-l3-iodaneyl)benzyl)-1H-benzo[d]imidazol-3-ium. Synthesised according to typical procedure B at 0.46 mmol

scale yielding the target compound as beige solids in 16% yield over 2 steps (35 mg, 0.73 mmol) as beige solids. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.41 (s, 1H), 7.78 – 7.71 (m, 2H), 7.70 – 7.63 (m, 1H), 7.47 – 7,43 (m, 1H), 7.36 – 7.28 (m, 2H), 7.21 – 7,17 (m, 2H), 5.56 (s, 2H), 1.54 (s, 6H). ^{13}C NMR (101 MHz, DMSO) δ 162.8, 144.2, 143.4, 139.8, 137.4, 132.9, 129.7, 122.5, 121.7, 119.5, 115.2, 110.6, 102.7, 57.9, 47.0, 25.6. HR-ESIMS: *m/z* 477.0306 $[M+H]^+$ ($C_{20}H_{18}IN_2O_4^+$, calculated 477.0306)

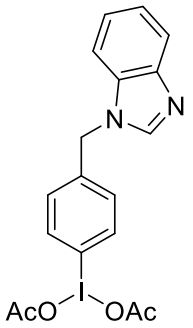


tert-butyl (3-(4-((2,2-dimethyl-4,6-dioxo-1,3-dioxan-5-ylidene)-l3-iodaneyl)phenoxy) -3-phenylpropyl)methylcarbamate. Reaction performed on 1.48 mmol scale yielding target compound in 45% yield (408 mg, 0.67 mmol) as brown solids.^{1}H NMR (400 MHz, DMSO-d_6) δ 7.64 – 7.56 (m, 2H), 7.40 – 7.30 (m, 4H), 7.28 – 7.22 (m, 1H), 6.99 – 6.90 (m, 2H), 5.34 (dt, *J* = 5.0, 2.6 Hz, 1H), 3.25 (broad s, 1H), 2.76 (s, 3H), 2.09 (dq, *J* = 13.9, 7.2 Hz, 1H), 1.98 (s, 1H), 1.52 (s, 6H), 1.38 – 1.17 (m, 9H). ^{13}C NMR (101 MHz, DMSO) δ 162.7, 159.3, 154.7, 140.5, 134.5, 128.6, 127.7, 126.0, 118.2, 105.8, 102.5, 78.4, 58.4, 54.9, 44.9, 38.9, 36.0, 33.7, 27.9, 25.5. HR-ESIMS: *m/z* 632.1115 $[M+Na]^+$ ($C_{27}H_{31}IN_2NaO_7^+$, calculated 632.1116).

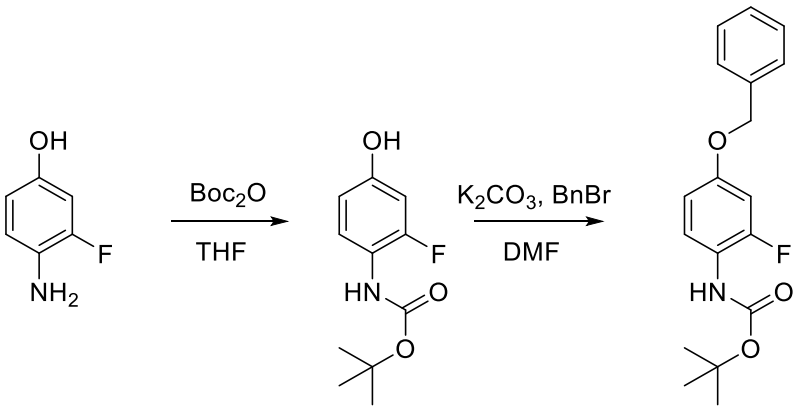


8-methyl-8-azabicyclo[3.2.1]octan-3-yl 4-((2,2-dimethyl-4,6-dioxo-1,3-dioxan-5-ylidene)-l3-iodaneyl)benzoate. To 8-methyl-8-azabicyclo[3.2.1]octan-3-yl 4-iodobenzoate (165 mg, 0.44 mmol) in $CHCl_3$ (1.5 ml) was added TFA (4 ml) and oxone monopersulphate (220 mg, 0.70 mmol) and left at room temperature for 3 hours. The solvent was removed over a stream of nitrogen and the residues dissolved in EtOH (5 ml) and pH adjusted to ~10 via addition of 10% w/v Na_2CO_3. 2,2-dimethyl-1,3-dioxane-4,6-dione (95mg, 0.66 mmol) was added from 10% w/v Na_2CO_3 (2 ml) and the reaction was left at room temperature for 50 minutes. The reaction mixture was poured into DCM (25 ml)

and extracted with 2x25 ml DCM. The combined organic phases were washed with 0.5M $Na_2S_2O_3$ and dried over sodium sulphate. The solvents were removed under reduced pressure and the crude dissolved in DCM and hexanes was added to induce precipitation. The cloudy suspension was subjected to freezer and the target compound (95 mg, 0.19 mmol) was afforded as white solids in 42% via filtration and washed with hexanes. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.99 – 7.94 (m, 4H), 5.12 (t, J = 5.2 Hz, 1H), 3.08 (broad s, 2H), 2.20 (s, 3H), 2.15 – 2.05 (m, 2H), 2.05 – 1.88 (m, 4H), 1.71 (d, J = 14.8 Hz, 2H), 1.58 (s, 6H). ^{13}C NMR (101 MHz, DMSO) δ 164.1, 162.8, 132.8, 132.2, 131.1, 121.3, 102.8, 68.6, 59.0, 58.0, 39.7, 35.7, 25.6, 25.6. HR-ESIMS: *m/z* 514.0721 $[M+H]^+$ ($C_{21}H_{25}INO_6^+$, calculated 514.0721).

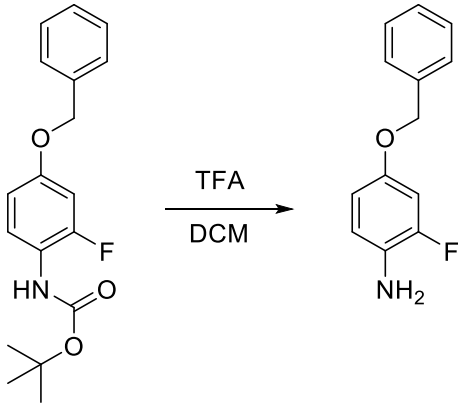


(4-((1H-benzo[d]imidazol-1-yl)methyl)phenyl)-l3-iodanediyl diacetate was (synthesised in accordance to[vi] affording the target compound in 77% (210 mg, 0.46 mmol) as white solids used for the next step without further purification**.** Analytical data was in accordance to that previously reported[vii]

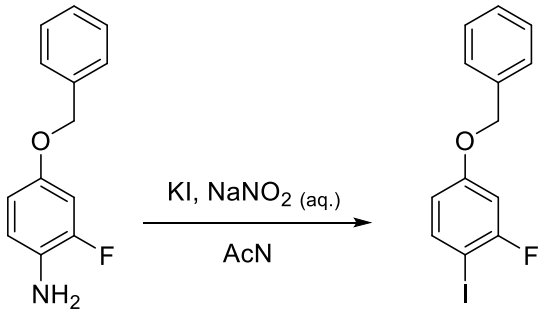


tert-butyl (4-(benzyloxy)-2-fluorophenyl)carbamate. To 4-amino-3-fluorophenol (5.59g, 44 mmol) in THF (40 ml) on ice was added di-*tert*-butyl dicarbonate (48.4 mmol, 10.6g) from THF (20 ml). The reaction mixture was stirred overnight. The solvents were removed under reduced pressure. The crude was dissolved in DCM and washed with water and aqueous sat. $NaHCO_3$. The organic phase was dried over sodium sulfate and evaporated to dryness under reduced pressure. The black crude was used in the next step without further purification.

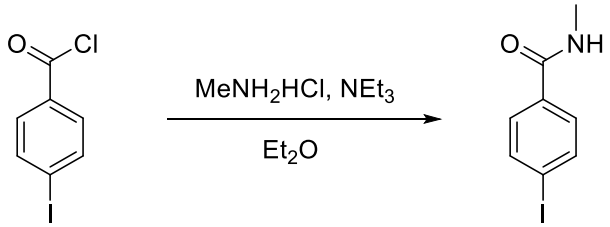
To the crude in DMF (30 ml) was added K_2CO_3 (9.12 g, 66 mmol) and benzyl bromide (5.23 ml, 50.8 mmol) and left over night. The crude was dissolved in DCM and washed with water. The organic phase was dried over sodium sulfate and evaporated to dryness under reduced pressure. The black crude was recrystallized from EtOH yielding the target compound (6.99 g, 22.0 mmol) as brown solids in 50% over 2 steps. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.88 (s, 1H), 7.45 – 7.30 (m, 5H), 6.77 – 6.69 (m, 2H), 6.46 (s, 1H), 5.02 (s, 2H), 1.52 (s, 9H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -129.2. ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.0 (d, $^3J_{CF}$ = 11 Hz), 153.2 (d, $^1J_{CF}$ = 244 Hz), 152.9, 128.8, 128.2, 127.6, 121.8 (broad), 120.2 (d, $^2J_{CF}$ = 11 Hz), 110.6 (d, $^4J_{CF}$ = 3 Hz), 102.9 (d, $^2J_{CF}$ = 23 Hz), 80.9, 70.7, 28.5. HR-ESIMS: *m/z* 340.1319 $[M+Na]^+$ ($C_{18}H_{20}FNNaO_3^+$, calculated 340.1319)



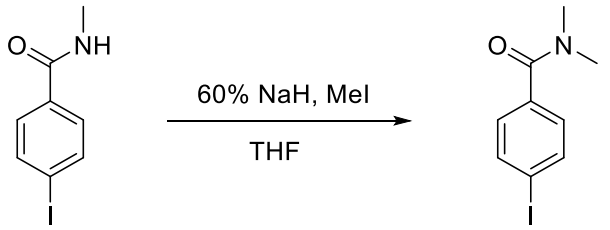
4-(benzyloxy)-2-fluoroaniline. To tert-butyl (4-(benzyloxy)-2-fluorophenyl)carbamate (6.41 g, 20.2 mmol) in DCM (45 ml) on ice was added dropwise trifluoroacetic acid (10 ml, 0.13 mol) and left for 4 hours. The crude was diluted with DCM and washed with aqueous sat. K_2CO_3. The organic phase was dried over sodium sulfate and evaporated to dryness under reduced pressure yielding the target compound (4.3 g, 19.8 mmol) in 98% as dark brown solids. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.45 – 7.29 (m, 5H), 6.78 – 6.66 (m, 2H), 6.61 (dd, *J* = 8.7, 2.9 Hz, 1H), 4.98 (d, *J* = 3.4 Hz, 2H), 3.41 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.07 (d, $^1J_{CF}$ = 239 Hz), 152.05 (d, $^3J_{CF}$ = 9 Hz), 137.1, 128.7, 128.2 (d, $^2J_{CF}$ = 13 Hz), 128.1, 127.6, 117.7 (d, $^3J_{CF}$ = 5 Hz), 111.1 (d, $^4J_{CF}$ = 3 Hz), 104.0 (d, $^2J_{CF}$ = 22 Hz), 71.0 ^{19}F NMR (376 MHz, Chloroform-*d*) δ -131.81 (dd, *J* = 12.4, 10.1 Hz). HR-ESIMS: *m/z* 218.0976 $[M+H]^+$ ($C_{13}H_{13}FNO^+$, calculated 218.0976)



4-(benzyloxy)-2-fluoro-1-iodobenzene To 4-(benzyloxy)-2-fluoroaniline (2.41 g, 11.1 mmol) in AcN (45 ml) on ice was added dropwise a solution of KI (4.6 g, 27.7 mmol) and $NaNO_2$ (1.53 g, 22.2 mmol) in water (8 ml). After effervescence had ceased the reaction mixture was allowed to reach room temperature and stirred for 1 hour. The reaction mixture was diluted with DCM and washed with water, 1M sodium thiosulfate and saturated $NaHCO_3$. The organic phase was dried over sodium sulfate and evaporated to dryness under reduced pressure. The crude was purified via flash column chromatography (0-20% DCM in hexanes) yielding the target compound (1.45 g, 4.43 mmol) in 40% as pale yellow oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.58 (dd, *J* = 8.7, 7.4 Hz, 1H), 7.45 – 7.33 (m, 4H), 6.74 (dd, *J* = 9.8, 2.8 Hz, 1H), 6.60 (ddd, *J* = 8.8, 2.8, 0.8 Hz, 1H), 5.04 (s, 2H). ^{19}F NMR (377 MHz, Chloroform-*d*) δ -92.05 (dd, *J* = 9.8, 7.3 Hz) ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.4 (d, $^1J_{CF}$ = 245 Hz), 160.6 (d, $^3J_{CF}$ = 10 Hz), 139.2 (d, $^3J_{CF}$ = 3 Hz), 136.1, 128.9, 128.4, 127.6, 113.2 (d, $^4J_{CF}$ = 3 Hz), 103.4 (d, $^2J_{CF}$ = 27 Hz), 70.61, 69.9 (d, $^2J_{CF}$ = 26 Hz) ^{19}F NMR (376 MHz, Chloroform-*d*) δ -131.81 (dd, *J* = 12.4, 10.1 Hz). HR-ESIMS: *m/z* 350.9653 $[M+Na]^+$ ($C_{13}H_{10}FINaO^+$, calculated 350.9653)

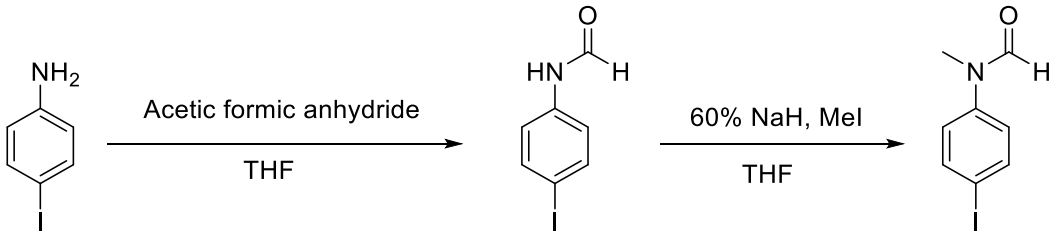


4-iodo-N-methylbenzamide. To 4-iodobenzoyl chloride (1 g, 3.75 mmol) in Et_2O was added methylamine hydrochloride (506 mg, 7.5 mmol) and triethylamine (1050 µl, 7.5 mmol). The reaction was left over night. The reaction mixture was diluted with Et_2O and washed with water. The organic phase was dried over sodium sulfate and solvents removed under reduced pressure. The crude was recrystallized from EtOAc yielding the target compound (793 mg, 3.04 mmol) in 81% as white solids. Analytical data was in accordance to that previously reported.[viii]



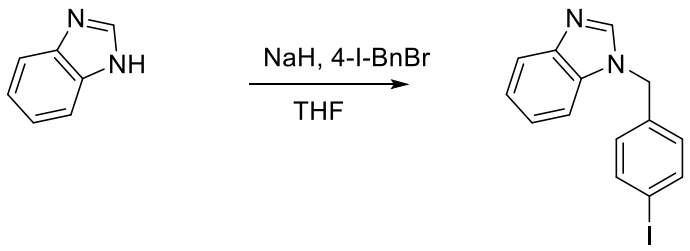
4-iodo-N,N-dimethylbenzamide. To 4-iodo-N-methylbenzamide (783 mg, 3mmol) in THF (10 ml) on ice was added 60% NaH in mineral oil (180 mg, 7.5 mmol) and left to stir for 30 minutes. Methyliodide (280 µl, 4.5 mmol) was added and the reaction mixture was allowed to reach room temperature and kept for 3 hours. The reaction mixture was evaporated to

dryness under reduced pressure. The crude was dissolved in Et_2O and washed with water and aqueous sat. $NaHCO_3$. The organic phase was dried over sodium sulfate and solvent removed under reduced pressure. The crude was purified via flash column chromatography (4% MeOH in DCM) affording the target compound (604 mg, 2.20 mmol) in 73% as white solids. Analytical data was in accordance to that previously reported.[ix]

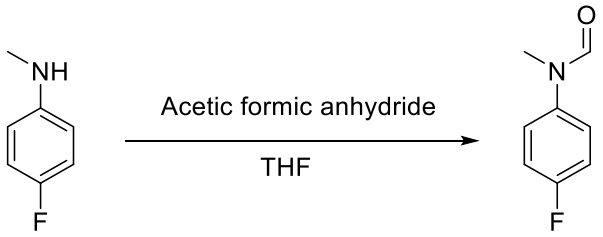


N-(4-iodophenyl)-N-methylformamide. Formic acid (1.30 ml, 34.3 mmol) was added to acetic anhydride (2.66 ml, 27.4 mmol) and heated at 65 °C for 30 minutes. The formed acetic formic anhydride solution was added drop wise to 4-iodoaniline (3 g, 13.7 mmol) in THF (5 ml) on ice. The reaction mixture was kept for 15 minutes and subsequently evaporated to dryness under reduced pressure. The crude was dissolved in EtOAc and washed with aqueous sat. $NaHCO_3$. The organic phase was evaporated to dryness under reduced pressure and the obtained beige solids (3.26 g) were used without further purification in the next step.

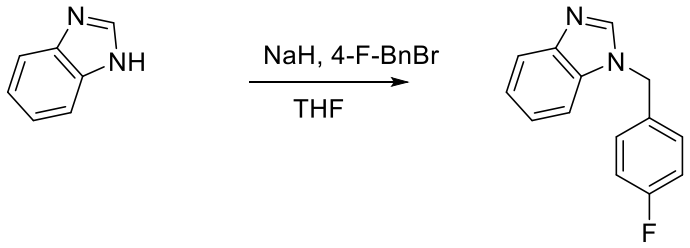
The crude was dissolved in THF (50 ml) and on ice was 60% NaH in mineral oil (822 mg, 20.6 mmol) added. The reaction was left to stir for 30 minutes prior to drop wise addition of MeI (1.28 ml, 20.6 mmol). The reaction mixture was allowed to reach room temperature and kept for 6 hours. The reaction mixture was evaporated to dryness under reduced pressure. The crude was dissolved in EtOAc and washed with water and brine. The organic phase was dried over sodium sulfate and evaporates to dryness under reduced pressure. The crude was purified via recrystallization from hexanes/chloroform affording the target compound (1.53g, 5.86 mmol) as purple-beige needles in 45% over two steps. Recording NMR spectra yielded a mixture of rotary isomers in 1:12. ^{1}H NMR (400 MHz, Chloroform-*d*) δ ((8.47, 8.37) (s, 1H)), (7.77 – 7.69 (m, 2H)), (7.27 – 7.23, 6.98 – 6.90 (m, 2H), (3.35, 3.30 (s, 3H)). ^{13}C NMR (101 MHz, $CDCl_3$) δ (162.1, 161.8), 142.0, (138.7, 138.0), (125.0, 123.9), 90.5, (36.4, 31.8). HR-ESIMS**:** *m/z* 283.9542 $[M+Na]^+$ ($C_8H_8INNaO^+$, calculated 283.9543)



1-(4-iodobenzyl)-1H-benzo[d]imidazole. To benzimidazole (708 mg, 6.0 mmol) in THF (30 ml) was added 60% NaH in mineral oil (360 mg, 9 mmol) and 4-iodobenzylbromide (1.78 g, 6.0 mmol). The reaction mixture was heated to 60 °C overnight. The reaction mixture was evaporated to dryness under reduced pressure. The crude was dissolved in EtOAc and extracted with water and brine. The organic phase was dried over sodium sulfate and evaporated to dryness under reduced pressure. The crude was purified via recrystallization from EtOH affording the target compound (1.71 g, 5.1 mmol) as white fluffy solids in 85%. Analytical data was in accordance to that previously reported[x] ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.95 (s, 1H), 7.89 – 7.82 (m, 1H), 7.72 – 7.62 (m, 2H), 7.35 – 7.21 (m, 3H), 6.97 – 6.88 (m, 2H), 5.31 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.2, 143.2, 138.3, 135.3, 133.9, 128.9, 123.4, 122.5, 120.7, 110.0, 93.9, 48.4. HR-ESIMS: *m/z* 335.0039 $[M+H]^+$ ($C_{15}H_{11}IN_2^+$, calculated 335.0040)

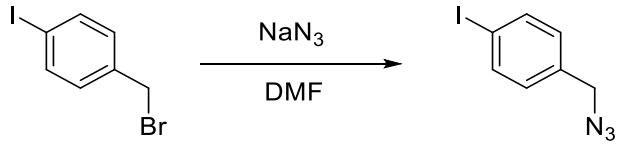


N-(4-fluorophenyl)-N-methylformamide. Formic acid (94 µl, 2.5 mmol) was added to acetic anhydride (189 µl, 2.0 mmol) and heated at 65 °C for 30 minutes. The formed acetic formic anhydride solution was added drop wise to4-fluoro-N-methylaniline (128µl, 1.06 mmol) in THF (1 ml) on ice. The reaction mixture was kept for 15 minutes and subsequently evaporated to dryness under reduced pressure. The crude was dissolved in EtOAc and washed with $NaHCO_3$. The organic phase was evaporated to dryness under reduced pressure. The crude was purified using flash column chromatography (0-2% MeOH in DCM) yielding the target compound (63 mg, 0.41 mmol) as yellow oil that solidified in 39%. Analytical data was in accordance to that previously reported.[xi]

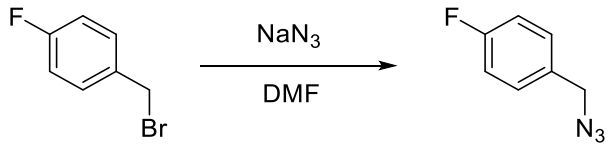


1-(4-fluorobenzyl)-1H-benzo[d]imidazole. To benzimidazole (354 mg, 3.0 mmol) in THF (15 ml) was added 60% NaH in mineral oil (180 mg, 4.5 mmol) and 4-fluorobenzylbromide (374 µl, 3.0 mmol). The reaction mixture was heated to 60 °C overnight. The reaction mixture was evaporated to dryness under reduced pressure. The crude was dissolved in EtOAc and extracted with water and brine. The crude was purified via flash column

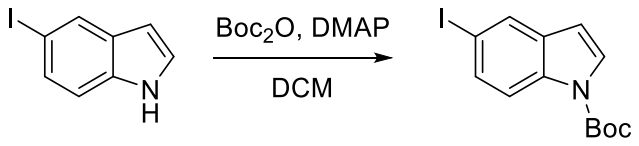
chromatography (4% MeOH in DCM) affording the target compound (544 mg, 2.4 mmol) as yellow oil in 80%. Analytical data was in accordance to that previously reported [xii]



1-(azidomethyl)-4-iodobenzene. To 1-(bromomethyl)-4-iodobenzene (5 mmol, 1.49 g) in DMF (7 ml) was added sodium azide (15 mmol, 975 mg) and left to stir over night. The reaction mixture was diluted with EtOAc and washed with water. The organic phase was dried over sodium sulphate and evaporated to dryness under reduced pressure. The crude was purified via flash column chromatography (10% EtOAc in hexanes) affording the target compound as white solids in 97% (1.25 g, 4.8 mmol). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.33 – 7.27 (m, 2H), 7.11 – 7.04 (m, 2H), 4.32 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.0, 161.6, 131.4, 131.3, 130.2, 130.1, 116.0, 115.8, 54.2. GC-MS *m/z* 258.9 [M] ($C_7H_6IN_3$, calculated 259.0).



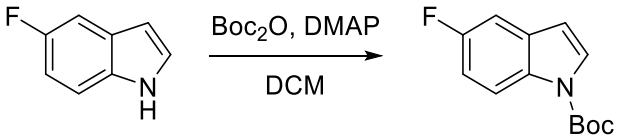
1-(azidomethyl)-4-iodobenzene. To 1-(bromomethyl)-4-fluorobenzene (0.2 mmol, 38 mg) in DMF (1 ml) was added sodium azide (0.6 mmol, 65 mg) and left to stir over night. The reaction mixture was diluted with EtOAc and washed with water. The organic phase was dried over sodium sulphate and evaporated to dryness under reduced pressure. The crude was purified via flash column chromatography (10% EtOAc in hexanes) affording the target compound in 93% as colourless oil (28 mg, 0.19 mmol). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.33 – 7.27 (m, 2H), 7.11 – 7.04 (m, 2H), 4.32 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.5 (d, $^{1}J_{CF}$ = 162 Hz), 131.3 ($^{4}J_{CF}$ = 3 Hz), 130.2 ($^{3}J_{CF}$ = 8 Hz), 116.0 ($^{4}J_{CF}$ = 22 Hz), 54.21. ^{19}F NMR (377 MHz, $CDCl_3$) δ -113.6. GC-MS *m/z* 151.0 [M] ($C_7H_6FN_3$, calculated 151.1).



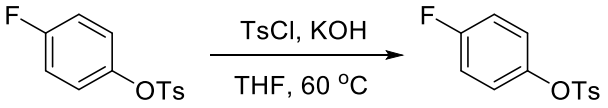
tert-butyl 5-iodo-1H-indole-1-carboxylate

To 5-iodo-1H-indole (972 mg, 4.0 mmol) in DCM (30 ml) was added Di-*tert*-butyl dicarbonate (1.05 g, 4.8 mmol) and N,N-dimethylpyridin-4-amine (98 mg, 0.8 mmol). The reaction mixture was left over night. The solvents were removed under reduced pressure

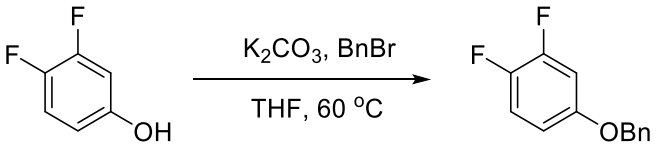
and the crude purified via flash column chromatography (5% EtOAc in hexanes) yielding the target compound as white solids in 75% (1140 mg, 3.3 mmol). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.94 – 7.88 (m, 2H), 7.57 (dd, *J* = 8.7, 1.8 Hz, 1H), 7.55 (d, *J* = 3.7 Hz, 1H), 6.49 (dd, *J* = 3.8, 0.8 Hz, 1H), 1.67 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.6, 134.6, 133.0, 132.8, 129.9, 126.8, 117.2, 106.4, 86.8, 84.3, 28.3. HR-ESIMS: *m/z* 365.9961 $[M+Na]^+$ ($C_{13}H_{14}INNaO_2^+$, calculated 365.9961)



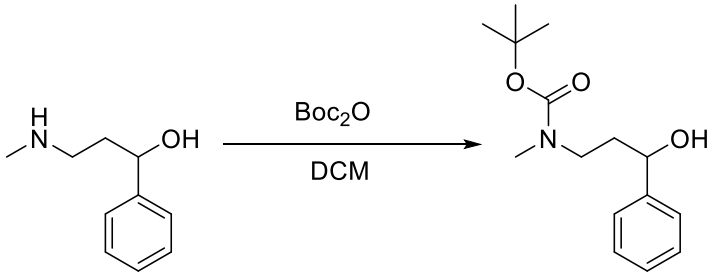
tert-butyl 5-fluoro-*1H*-indole-1-carboxylate. To 5-fluoro-*1H*-indole (68 mg, 0.5 mmol) in THF (5 ml) was added Di-*tert*-butyl dicarbonate (131 mg, 0.6 mmol) and DMAP (6 mg, 0.05 mmol). The reaction kept overnight. The solvent was removed under reduced pressure and the crude purified via flash column chromatography (5% EtOAc in hexanes) affording the target compound as white solids (96 mg, 0.41 mmol) in 82%. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.09 (s, 1H), 7.62 (d, *J* = 3.7 Hz, 1H), 7.21 (dd, *J* = 8.8, 2.6 Hz, 1H), 7.03 (td, *J* = 9.1, 2.6 Hz, 1H), 6.52 (dd, *J* = 3.7, 0.7 Hz, 1H), 1.67 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.3 ($^{1}J_{CF}$ = 239 Hz), 149.7, 131.7, 131.5 ($^{3}J_{CF}$ = 10 Hz), 127.6, 116.2 ($^{3}J_{CF}$ = 9 Hz), 112.1 ($^{2}J_{CF}$ = 25 Hz), 107.1 ($^{4}J_{CF}$ = 4 Hz), 106.5 ($^{2}J_{CF}$ = 24 Hz), 84.0, 28.3. ^{19}F NMR (377 MHz, $CDCl_3$) δ -121.3. HR-ESIMS: *m/z* 258.0900 $[M+Na]^+$ ($C_{13}H_{14}FNNaO_2^+$, calculated 258.0901).



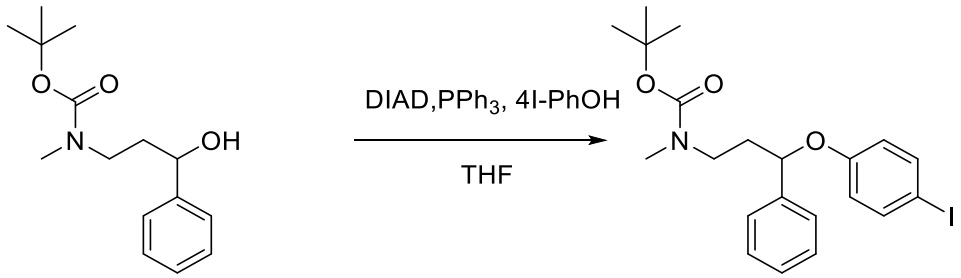
4-fluorophenyl 4-methylbenzenesulfonate. To 4-fluorophenol (2.24 g, 20mmol) in THF (50 ml) was added 4-methylbenzenesulfonyl chloride (4.19 g, 22 mmol) and potassium hydroxide (225 mg, 2.24 mmol). The reaction was heated at 60 degrees overnight. The reaction mixture was diluted with ethyl acetate and washed with water. The organic phase was dried over sodium sulphate and evaporated to dryness under reduced pressure. The crude was purified via recrystallization from EtOH (15 ml) at -20 °C afforded the target compound as white needles in 45% (2.42 g, 9.1 mmol). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.73 – 7.65 (m, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.00 – 6.91 (m, 4H), 2.45 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.4, 159.9, 145.7, 145.6, 145.5, 132.2, 129.9, 128.7, 124.2, 124.1, 116.6, 116.3, 21.9. 161.1 ($^{1}J_{CF}$ = 247 Hz), 145.7, 145.5 ($^{4}J_{CF}$ = 3 Hz), 132.2, 130.0, 128.7, 124.2 ($^{3}J_{CF}$ = 9 Hz), 116.5 ($^{2}J_{CF}$ = 24 Hz), 21.9. ^{19}F NMR (377 MHz, Chloroform-*d*) δ -114.6 HR-ESIMS: *m/z* 289.0306 $[M+Na]^+$ ($C_{13}H_{11}FNaO_3S^+$, calculated 289.0305).



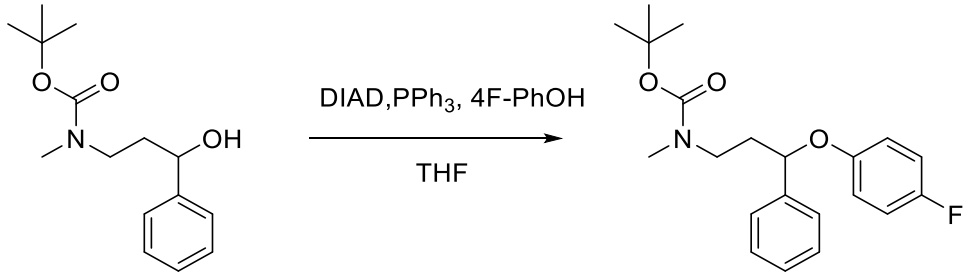
4-(benzyloxy)-1,2-difluorobenzene. To 3,4-difluorophenol (650 mg, 5 mmol) in THF (5 ml) was added potassium carbonate (690 mg, 5 mmol) and benzyl bromide (0.60 ml, 5.25 mmol). The reaction was left at 60 degrees for 5 days. Additional benzyl bromide (0.60 ml, 5.25 mmol) was added and the reaction left for 5 more days. The reaction mixture was diluted with diethyl ether and washed repeatedly with water. The organic phase was dried over sodium sulphate and evaporated to dryness under reduced pressure. The crude was purified via flash column chromatography (0-15% EtOAc in hexanes) affording the target compound as white solids in 51% (570 mg, 2.6 mmol). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.44 – 7.31 (m, 5H), 7.06 (dt, *J* = 10.1, 9.1 Hz, 1H), 6.79 (ddd, *J* = 12.0, 6.5, 3.0 Hz, 1H), 6.67 (dtd, *J* = 9.1, 3.2, 1.8 Hz, 1H), 5.02 (s, 2H). ^{19}F NMR (377 MHz, Chloroform-*d*) δ –135.5 (d, *J* = -22 Hz), –148.1 (d, *J* = -22 Hz). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.2 ($^{3,4}J_{CF}$ = 9, 2 Hz), 150.6 ($^{1,2}J_{CF}$ = 248, 14 Hz), 145.3 ($^{1,2}J_{CF}$ = 241, 13 Hz), 136.4, 128.8, 128.4, 127.6, 117.3 ($^{2,3}J_{CF}$ = 19, 2 Hz), 110.3 ($^{3,4}J_{CF}$ = 6, 4 Hz), 104.7 ($^{3}J_{CF}$ = 20 Hz), 71.0.



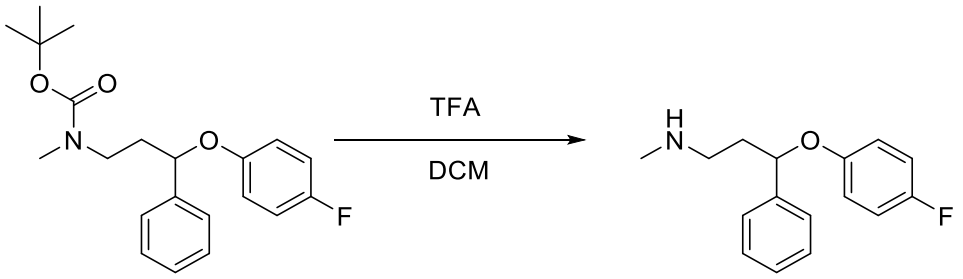
tert-butyl (3-hydroxy-3-phenylpropyl)(methyl)carbamate. To 3-(methylamino)-1-phenylpropan-1-ol (1.65 g, 10 mmol) in DCM (25 ml) on ice was added di-tert-butyl dicarbonate (2.18 g, 10 mmol) and stirred for 2 hours at room temperature. The solvents were removed under reduced pressure and the crude dissolved in diethyl ether (200 ml) and washed with 0.5 M aqueous HCl (50 ml) and brine. The organic phase was dried over sodium sulphate and evaporated to dryness under reduced pressure affording the desired product as colourless oil in 93% (2.48 g, 9.3 mmol). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.44 – 7.30 (m, 4H), 7.25 (t, *J* = 7.2 Hz, 1H), 4.60 (s, 1H), 3.92 (s, 1H), 3.04 (s, 1H), 2.87 (s, 3H), 1.95 (dddd, *J* = 13.8, 9.9, 6.1, 3.5 Hz, 1H), 1.77 (s, 1H), 1.47 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.3, 144.3, 128.5, 127.3, 125.8, 80.2, 70.1, 45.4, 37.4, 34.4, 28.6. HR-ESIMS: *m/z* 288.1570 $[M+Na]^+$ ($C_{15}H_{23}NNaO_3^+$, calculated 288.1570).



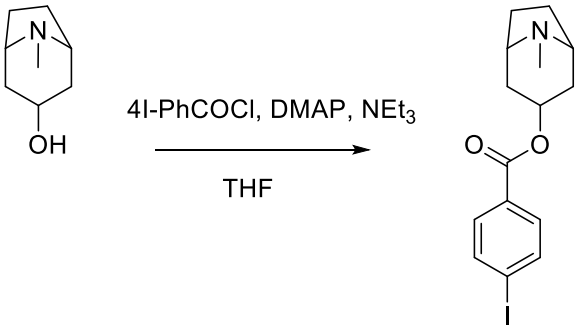
tert-butyl (3-(4-iodophenoxy)-3-phenylpropyl)(methyl)carbamate. To triphenylphosphane (1640 mg, 6.3 mmol) in THF (20 ml) on ice was dropwise added diisopropyl azodicarboxylate (1100 µl, 5.6 mmol). After 20 minutes was added 4-iodophenol (1265 mg, 5.75 mmol) from THF (10 ml) and tert-butyl (3-hydroxy-3-phenylpropyl)(methyl)carbamate (1110 mg, 4.2 mmol) from THF (15 ml). The reaction was allowed to reach room temperature and left over night. Solvents were removed under reduced pressure and the crude purified using flash column chromatography (15% EtOAc in hexanes) affording the product as colourless oil in 75% (1250 mg, 4.7 mmol). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.57 – 7.47 (m, 2H), 7.43 – 7.30 (m, 5H), 6.75 – 6.61 (m, 2H), 5.14 (dd, *J* = 8.5, 4.2 Hz, 1H), 3.63 – 3.30 (m, 2H), 2.92 (s, 3H), 2.21 (br. s, 1H), 2.13 (dtd, *J* = 13.8, 7.7, 4.1 Hz, 1H), 1.47 (s, 9H($^{1}J_{CF}$ = 247 Hz), 158.0, 155.9, 141.2, 138.2, 128.9, 127.9, 125.8, 118.4, 83.0, 79.6, 77.7, 45.9, 37.3, 34.7, 28.5. HR-ESIMS: *m/z* 490.0850 $[M+Na]^{+}$ ($C_{21}H_{26}INNaO_3^{+}$, calculated 490.0850).



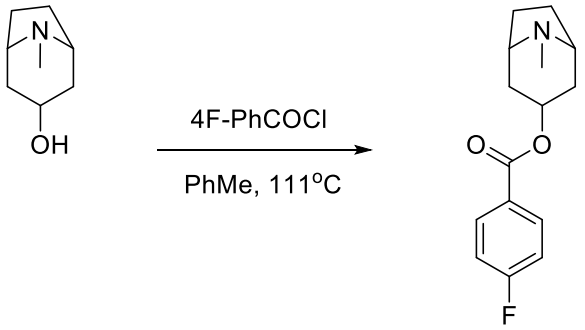
tert-butyl (3-(4-fluorophenoxy)-3-phenylpropyl)(methyl)carbamate. To triphenylphosphane (354 mg, 1.35 mmol) in THF (5 ml) on ice was dropwise added diisopropyl azodicarboxylate (237 µl, 1.21 mmol). After 40 minutes was added 4-fluorophenol (150 mg, 1.34 mmol) from THF (2 ml) and tert-butyl (3-hydroxy-3-phenylpropyl)(methyl)carbamate (240 mg, 0.90 mmol) from THF (5 ml). The reaction was allowed to reach room temperature and left over night. Solvents were removed under reduced pressure and the crude purified using flash column chromatography (15% EtOAc in hexanes) affording the product as pale pink oil in 50% (163 mg, 0.45 mmol). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.36 – 7.29 (m, 4H), 7.28 – 7.22 (m, 1H), 6.88 – 6.81 (m, 2H), 6.78 – 6.71 (m, 2H), 5.03 (dd, *J* = 8.7, 4.1 Hz, 1H), 3.52 – 3.24 (m, 2H), 2.84 (s, 3H), 2.13 (s, 1H), 2.05 (dtd, *J* = 13.9, 7.7, 4.1 Hz, 1H), 1.39 (s, 9H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -123.9. ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.3 ($^{1}J_{CF}$ = 238 Hz), 155.9, 154.2, 141.6, 128.9, 127.9, 125.9, 117.0, 115.8 ($^{2}J_{CF}$ = 23 Hz), 79.5, 78.2, 46.0, 37.3, 34.7, 28.5. HR-ESIMS: *m/z* 382.1789 $[M+Na]^{+}$ ($C_{21}H_{26}FNNaO_3^{+}$, calculated 382.1789).



3-(4-fluorophenoxy)-N-methyl-3-phenylpropan-1-amine. To tert-butyl (3-(4-fluorophenoxy)-3-phenylpropyl)(methyl)carbamate (145 mg, 0.40 mmol) in DCM (5 ml) was added TFA (1 ml) and left at room temperature for 6 hours. The reaction mixture was diluted with DCM and washed with 14% ammonia and brine. The organic phase was dried over sodium sulphate and evaporated to dryness under reduced pressure. The crude was purified via flash column chromatography (8-20% MeOH in DCM) affording the target compound as pale yellow oil (41 mg, 0.16 mmol) in 40%. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.47 – 7.11 (m, 5H), 6.95 – 6.59 (m, 4H), 5.16 (dd, *J* = 8.3, 4.7 Hz, 1H), 2.76 (t, *J* = 7.4 Hz, 2H), 2.44 (s, 3H), 2.18 (dq, *J* = 14.3, 7.1 Hz, 1H), 2.00 (ddt, *J* = 14.2, 7.2, 3.6 Hz, 1H), 1.94 (broad s, 1H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -123.8. ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.3 ($^{1}J_{CF}$ = 239 Hz), 154.3 ($^{4}J_{CF}$ = 2 Hz), 141.7, 128.8, 127.8, 126.1, 117.2 ($^{3}J_{CF}$ = 8 Hz), 115.8 ($^{2}J_{CF}$ = 23 Hz), 79.4, 48.5, 38.7, 36.5.



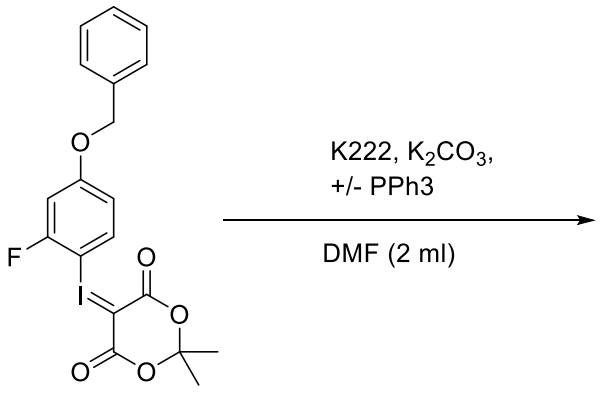
8-methyl-8-azabicyclo[3.2.1]octan-3-yl 4-iodobenzoate. To Tropine (564 mg, 4.4 mmol) in THF (40 ml) was added triethylamine (556 µl, 4.0 mmol), DMAP (24 mg, 0.2 mmol) and 4-iodobenzoyl chloride (1066 mg, 4 mmol) and left over night at room temperature. The crude was diluted with DCM, washed with sat. $NaHCO_3$ and brine. The solvents were removed under reduced pressure and the crude purified via flash column chromatography (8-25% MeOH in DCM) affording the target compound (290 mg, 0.78 mmol) as white solids in 20%. ^{1}H NMR (400 MHz, Methanol-d_4) δ 7.96 – 7.83 (m, 2H), 7.79 – 7.72 (m, 2H), 5.20 (t, *J* = 5.3 Hz, 1H), 3.29 – 3.24 (m, 2H), 2.37 (s, 3H), 2.25 (dt, *J* = 15.5, 4.6 Hz, 2H), 2.21 – 2.07 (m, 4H), 1.95 – 1.83 (m, 2H). ^{13}C NMR (101 MHz, MeOD) δ 166.7, 148.6, 139.2, 131.8, 131.4, 101.6, 69.1, 61.3, 40.3, 36.9, 26.4. HR-ESIMS: *m/z* 372.0455 $[M+H]^+$ ($C_{15}H_{19}INO_2^+$, calculated 372.0455).



8-methyl-8-azabicyclo[3.2.1]octan-3-yl 4-fluorobenzoate. To Tropine (282 mg, 2.0 mmol) in PhMe (2 ml) at reflux was added 4-iodobenzoyl chloride (260 µl, 2.2 mmol) and kept for 5.5 hours. The crude was diluted with DCM, washed with sat. $NaHCO_3$ and brine. The solvents were removed under reduced pressure and the crude purified via flash column chromatography (0-25% MeOH in DCM) affording the target compound (212 mg, 0.81 mmol) as white solids in 40%. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.05 – 7.96 (m, 2H), 7.18 – 7.09 (m, 2H), 5.33 (t, *J* = 5.2 Hz, 1H), 3.51 (s, 2H), 2.71 (s, 2H), 2.57 (s, 3H), 2.25 (s, 4H), 2.00 (d, *J* = 15.5 Hz, 2H). ^{19}F NMR (377 MHz, Chloroform-*d*) δ -105.12 (s).
^{13}C NMR (101 MHz, $CDCl_3$) δ 166.0 ($^1J_{CF}$ = 255 Hz), 164.7, 132.0 ($3J_{CF}$ = 9 Hz,), 126.6 ($^4J_{CF}$ = 3 Hz), 115.9 ($^1J_{CF}$ = 22 Hz), 66.9, 61.0, 39.6, 35.5, 25.4.HR-ESIMS: *m/z* 264.1394 $[M+H]^+$ ($C_{15}H_{19}FNO_2^+$, calculated 264.1394).

Kinetic NMR and radiotracer experiments

An NMR analysis of the reaction complemented HPLC and radioHPLC analysis. The product profile was recorded over minutes in presence and absence of catalyst to structurally identify each side product.

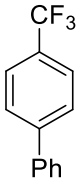


9.54 mg, 20 µmol

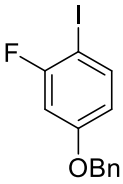
A V-bottomed vial was charged with K-222 (20 mg, 53 µmol) and K_2CO_3 x 1.5 H_2O (3.68 mg, 22.2 µmol) in 30/70 water/acetonitrile (1 ml). The vial was heated at 85°C under a stream of nitrogen. After evaporation of bulk solvents, AcN (1 ml) was added. The process was repeated 2 consecutive times. After the capped vial had cooled to room temperature, 5-((4-(benzyloxy)-2-fluorophenyl)-l3-iodaneylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (9.54

mg, 20 µmol), 4-trifluoromethylbiphenyl (~2 mg, 9 µmol) and PPh_3 (0 or 20 µmol) was added from DMF (2 ml). The vial placed on a heating block at 130 ^{o}C. Samples of 250 µl were taken at the following time points 0, 2, 3, 4, 6, 10 and 20 minutes and transferred to an NMR tube on ice in the dark. The samples were diluted with 350 µl of DMSO-d6 and analysed via ^{1}H and ^{19}F NMR.

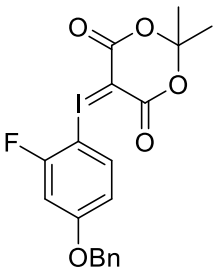
^{19}F-NMR Chemical shift in DMSO-d6



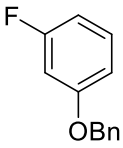
-61.6 ppm



-93.7 ppm



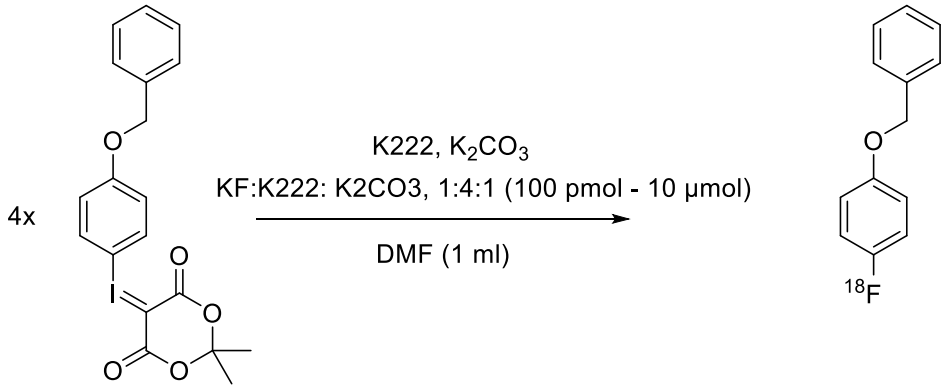
-96.9 ppm



-112.3 ppm

6. Carrier added experiments

A concentration dependent experiment was conducted to determine the molar conversion of precursor as a function of amount of substance of fluoride ion.



A V vial was charged with crypt-222 (40 mg, 106 µmol) and K_2CO_3 (7.36 mg, 44.4 µmol) in 30/70 water/acetonitrile (1 ml) containing ^{18}F-activity. The vial was heated at 85°C under a stream of nitrogen. After evaporation of bulk solvents 4 µM – 40 mM KF:K222: K_2CO_3, 1:4:1 (100 µl (1000 µl for 40 µmol addition)) in 30/70 water/acetonitrile (1 ml) and AcN (1 ml) was added. The drying process was repeated 2 consecutive times. The dried contents of the vial was dissolved in DMF (2000 µl) and distributed equally into 4 vials. 5-((4-(benzyloxy)phenyl)-l3-iodaneylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (4.52 mg, 10 µmol) and PPh_3 (0 or 2.62 mg, 10 µmol) was added from stock in DMF (500 µl). The vials were capped and heated in a heating block at 130 °C for 20 minutes. The reaction mixture was analysed via radioTLC.

Table S3: Yield of the aryl fluoride formation over 20 minutes in absence and presence of PPh_3.

$[F^-]^a$ mol/L	RCY[b] / % control	control	Average	Standard deviation
1,3E-05	44	50	47	3
1,86E-05	38	43	41	3
2,4E-05	52	43	47	4
0,000112	33	35	34	1
0,001	17	19	18	1
0,01	4	9	6	2
0,1	0	0	0	0
1	0	0	0	0
$[F^-]^a$ mol/L	RCY[b] / % +PPh3	+PPh3	Average	Standard deviation
1,3E-05	63	61	62	1
1,86E-05	60	36	48	12

2,4E-05	52	58	55	3
0,000112	58	63	60	2
0,001	64	64	64	0
0,01	43	47	45	2
0,1	20	19	20	1
1	5	5	5	0

a) ^{18}F chemical activity/concentration; b) Radiochemical yield in %

7. NMR experiments – fluorination under stoichiometric conditions

In order to investigate the educt and product distribution over time, serial NMR experiments were conducted. These experiments would not only allow for an analysis of the effect of triphenyl phosphine and degassing, respectively, but also decouple our previous experiences from no-carrier-added radiochemistry conditions.

To CsF (3.0 – 17 mg, 20 - 110 µmol) was added **5-((4-(benzyloxy)-2-fluorophenyl)-l3-iodaneylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione** (4.70 mg, 10 µmol) and 4-trifluoromethylbiphenyl (~0.5 mg, 2.5 µmol) from DMF (0.5 ml) and PPh3 (0 – 2.62 mg, 10 µmol). The reaction mixture was heated for 20-30 minutes at 130-150 °C. A portion of the reaction mixture (300 µl) was transferred to an NMR tube and 300 µl of DMSO-d6 was added. The reactions were analysed via ^{19}F-NMR analysis.

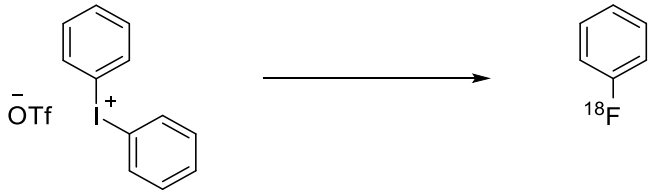
8. Origin of reduced side products: Alkene migration experiment

Deiodinated arenes were observed as major side products both by HPLC and NMR, respectively. These may indicate the presence of radicals in the reaction mixture. To test if this major non-radioactive side product was indeed formed via hydrogen abstraction by a putative arene-radical intermediate, we decided to employ a radical indicator. In brief, 4-allyl anisol was used to reveal unpaired electrons via radical induced migration of the double bond.

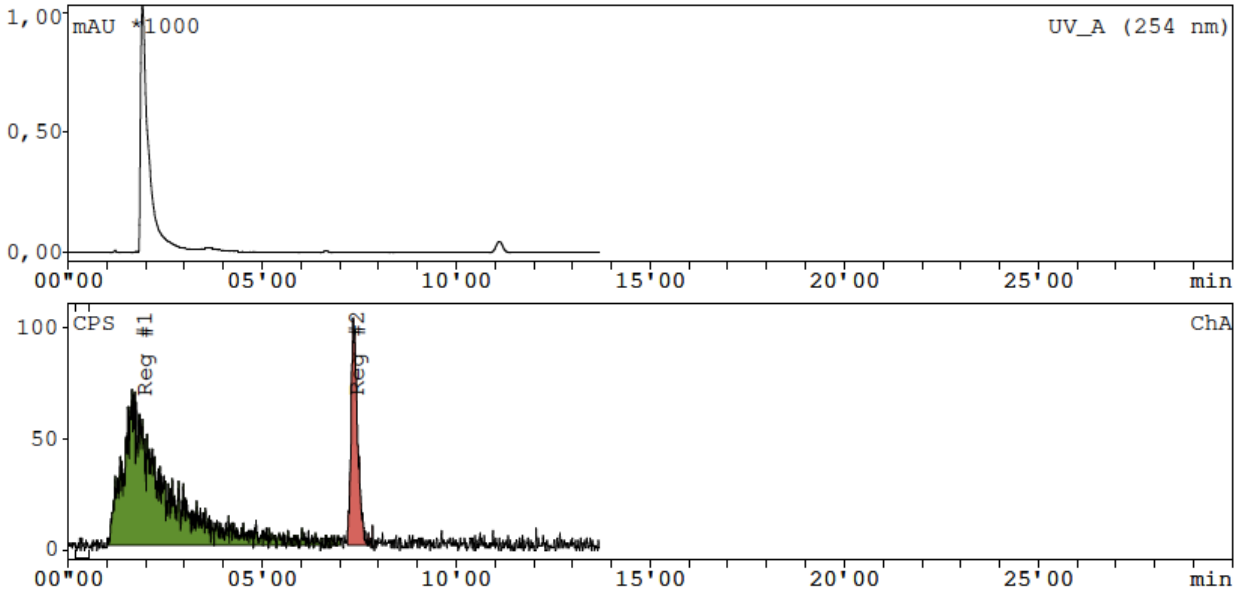
To **5-((4-(benzyloxy)phenyl)-l3-iodaneylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione** (9mg, 20µmol) in DMF (1 ml) was added 1-allyl-4-methoxybenzene (20 µmol, 3 mg) and heated at 130 degrees for 20 mintues. A small sample was withdrawn for crude NMR and the remains were diluted with ether (10 ml) and poured into water (10 ml). The phases were separated. The organic phase was dried over sodium sulphate and the bulk solvent removed under reduced pressure. The crude was analysed via NMR.

Despite several attempts, no double-bond migration was apparent under our reaction conditions.

9. HPLC chromatograms for selected experiments



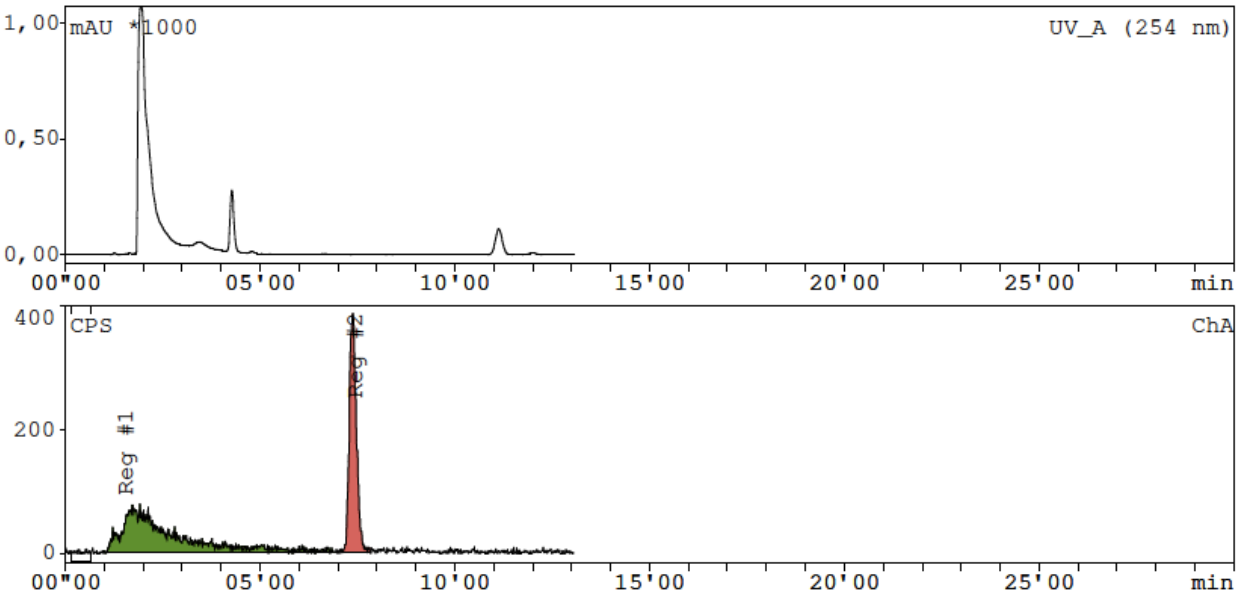
Standard procedure:



Integration ChA

Substance	R/T s	Type	Area Counts	%Area %
Reg #1	01'39	DD(M	4863,791	80,71
Reg #2	07'22	DD(M	1162,639	19,29
Sum in ROI			6026,430	100,00
Area (total)			6222,328	
BKG1			2,3383	

Standard procedure + 100 mol% PPh_3 + 1 min N_2

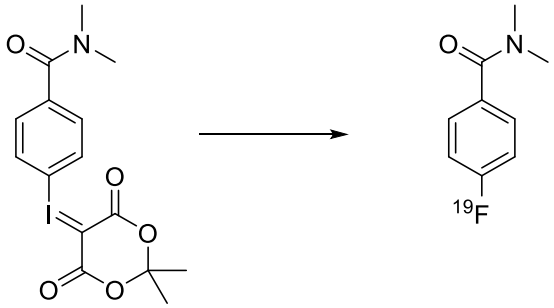


Integration ChA

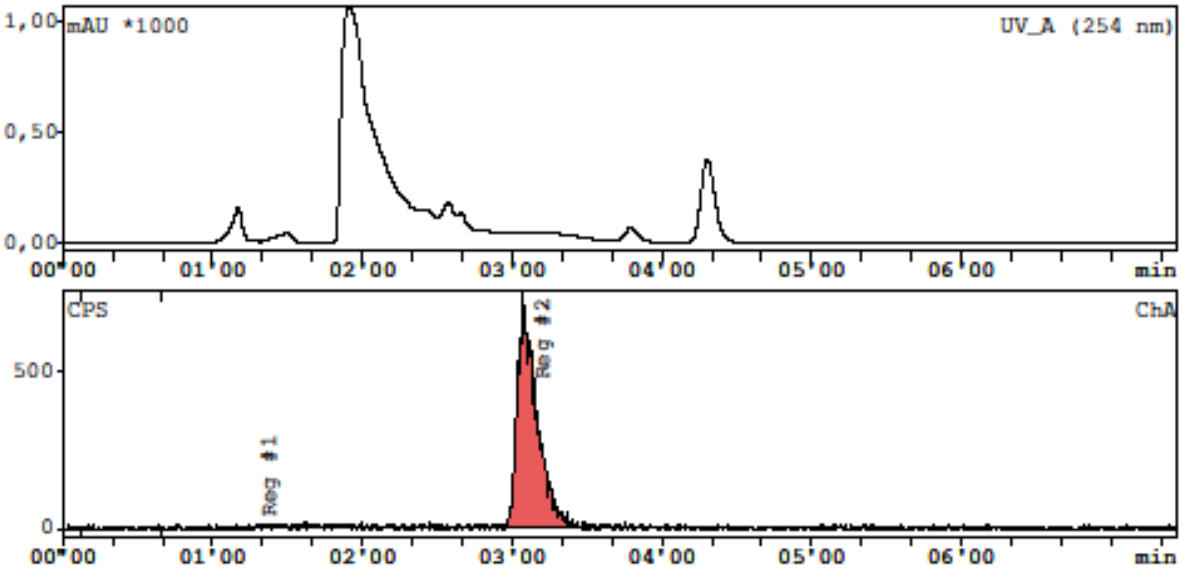
Substance	R/T s	Type	Area Counts	%Area %
Reg #1	01'43	DD(M	6352,549	57,17
Reg #2	07'23	DD(M	4759,193	42,83
Sum in ROI			11111,742	100,00
Area (total)			11532,535	
BKG1			2,4579	

Entry	RCC Conditions	Average RCC	Standard deviation	Repetitions
1	8,70	42,80	19,20	9,60
2	5,80	38,20	14,50	13,10
3	19,30	16,40		
4	6,70	19,20		

Entry	Conditions	RCC	Standard deviation	Repetitions
1	control	10	5	4
2	+PPh3	29	12	4
3	$+N_2$	17	2	2
4	+PPh3, +N2	11	2	2

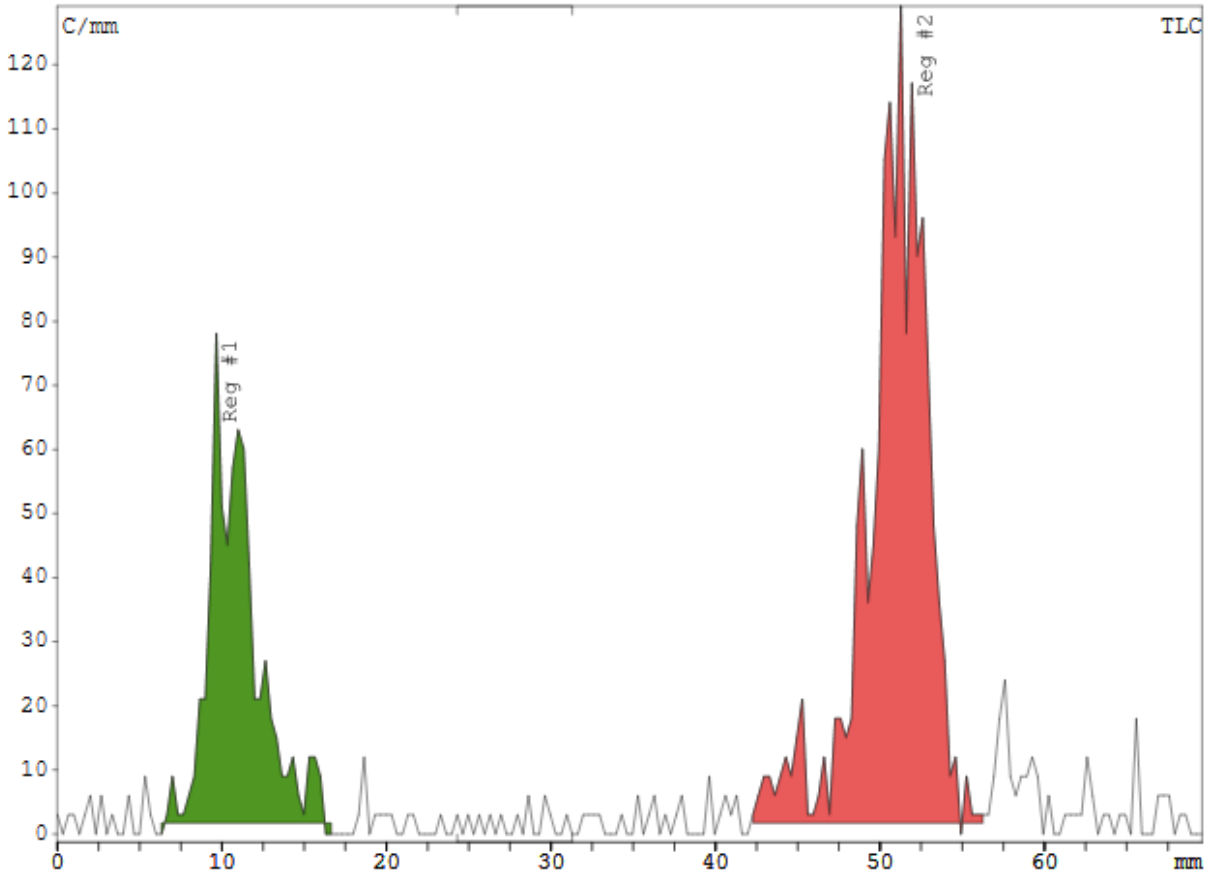


Standard procedure + 100 mol% PPh_3



Integration ChA

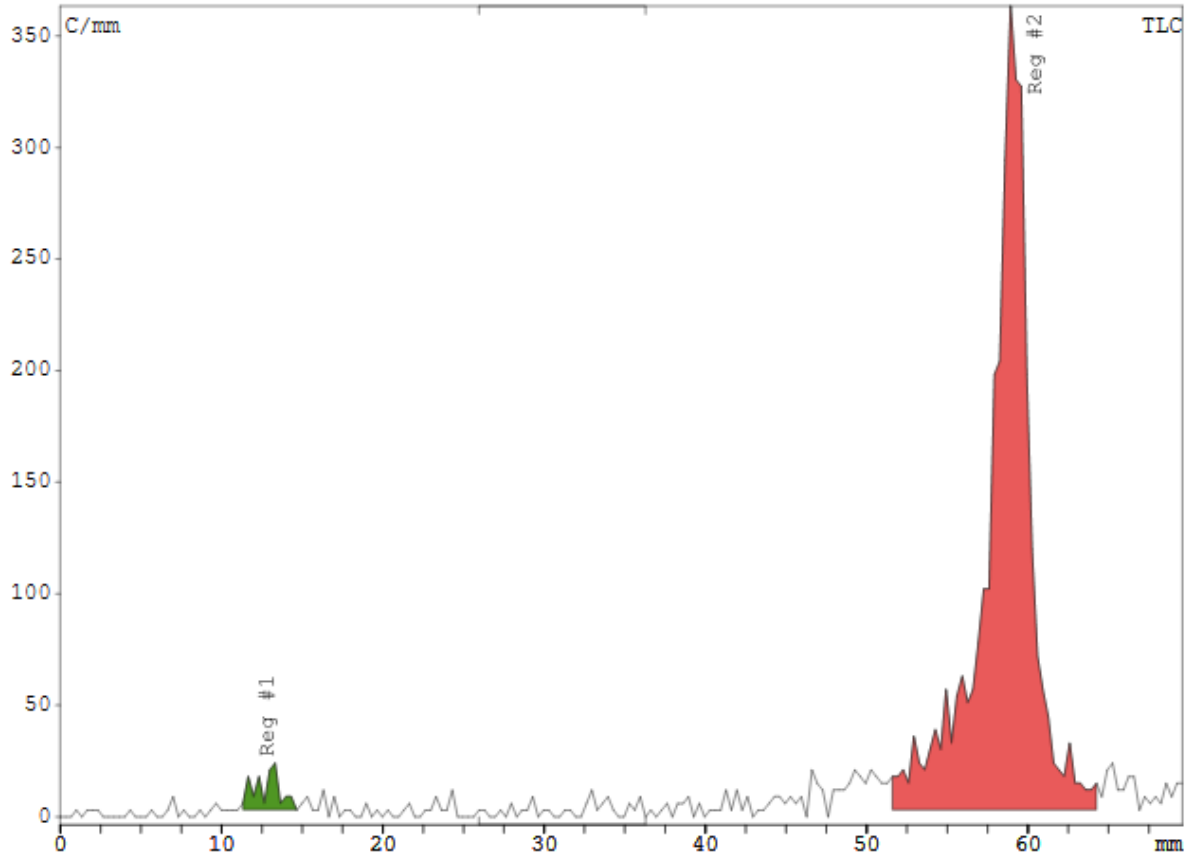
Substance	R/T s	Type	Area Counts	%Area %
Reg #1	01'22	DD(M	380,594	5,37
Reg #2	03'05	DD(M	6701,007	94,63
Sum in ROI			7081,602	100,00
Area (total)			7213,715	
BKG1			2,0872	
Remainder			132,11	1,83



Integration TLC

Substance	R/F	%Total	Type	Area	%Area
		%		Counts	%
Reg #1	0,148	28,80	DD	211,2857	30,97
Reg #2	0,733	64,21	DD	471,0000	69,03
Sum in ROI				682,2857	
Total area				733,5714	
Area RF				733,0000	
BKG1				1,71641	
Remainder RF				50,71	6,92
Remainder (Tot)				51,29	6,99

Standard procedure + 100 mol% PPh_3 + N_2



Integration TLC

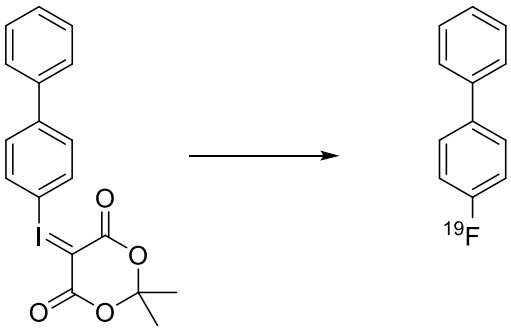
Substance	R/F	%Total	Type	Area	%Area
		%		Counts	%
Reg #1	0,181	2,69	DD	31,355	2,96
Reg #2	0,843	88,25	DD	1028,548	97,04
Sum in ROI				1059,903	
Total area				1165,516	
Area RF				1169,452	
BKG1				3,1975	
Remainder RF				109,55	9,37
Remainder (Tot)				105,61	9,06

RCC

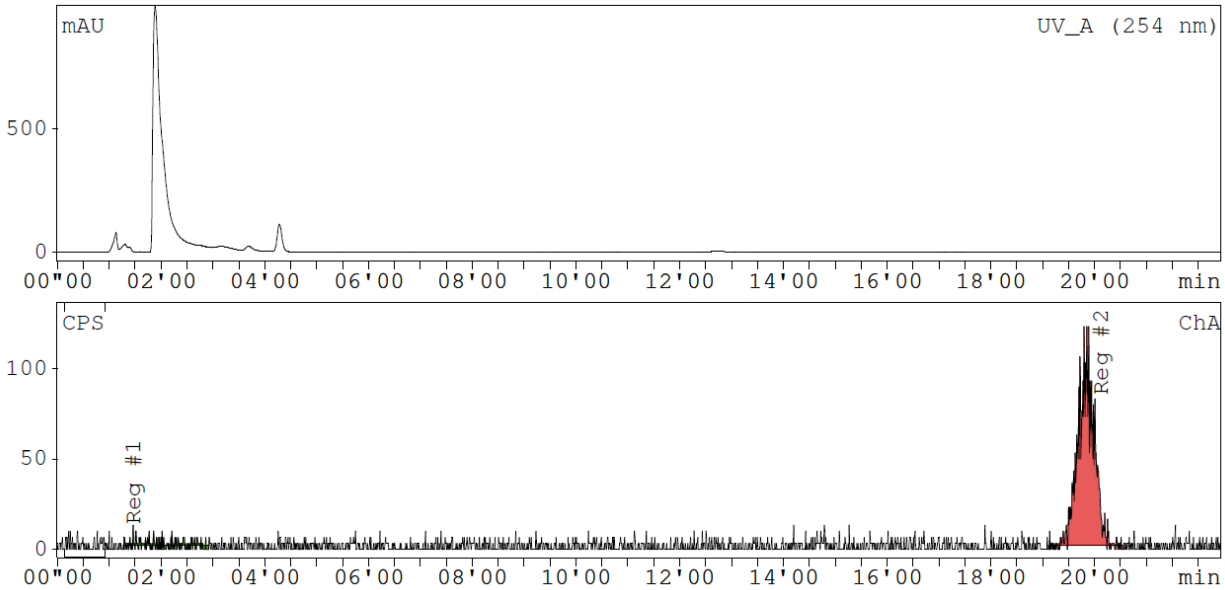
Entry	control	+PPh3	+N2	+PPh3, +N2
1	37,40	93,30	83,10	96,40

2	59,30	94,10	83,10	97,00
3	71,30	92,50		
4	72,40	96,90		
5	89,20	92,40		
	69,00			

Entry	**Conditions**	**Average RCC**	**Standard deviation**	**Repetitions**
1	control	66	16	6
2	+PPh3	94	2	5
3	$+N_2$	83	0	2
4	+PPh3, +N2	97	0	2



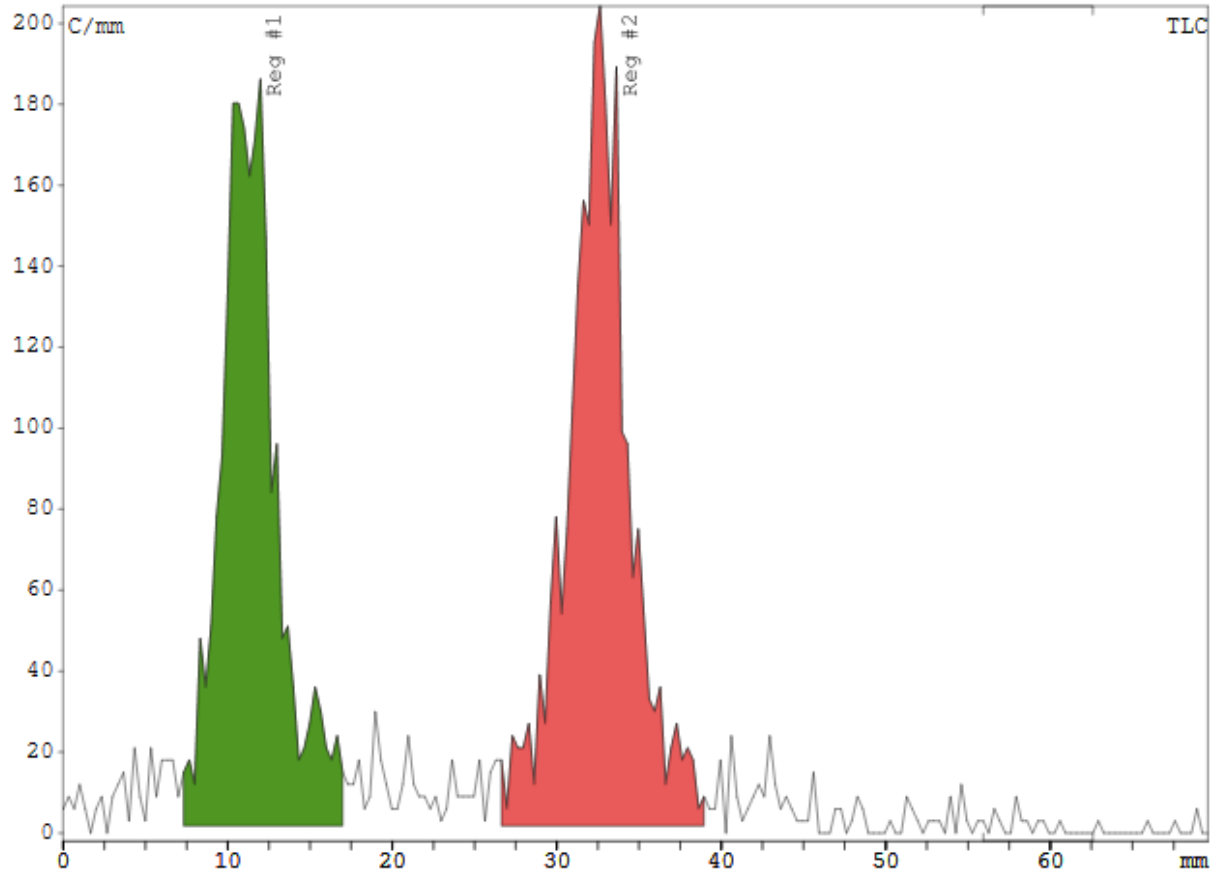
Standard procedure + 100 mol% PPh_3



Integration ChA

Substance	R/T s	Type	Area Counts	%Area %
Reg #1	01'32	DD(M	39,212	1,72
Reg #2	19'48	DD(M	2235,758	98,28
Sum in ROI			2274,970	100,00
Area (total)			1894,833	
BKG1			2,2436	
Remainder			-380,14	-20,06

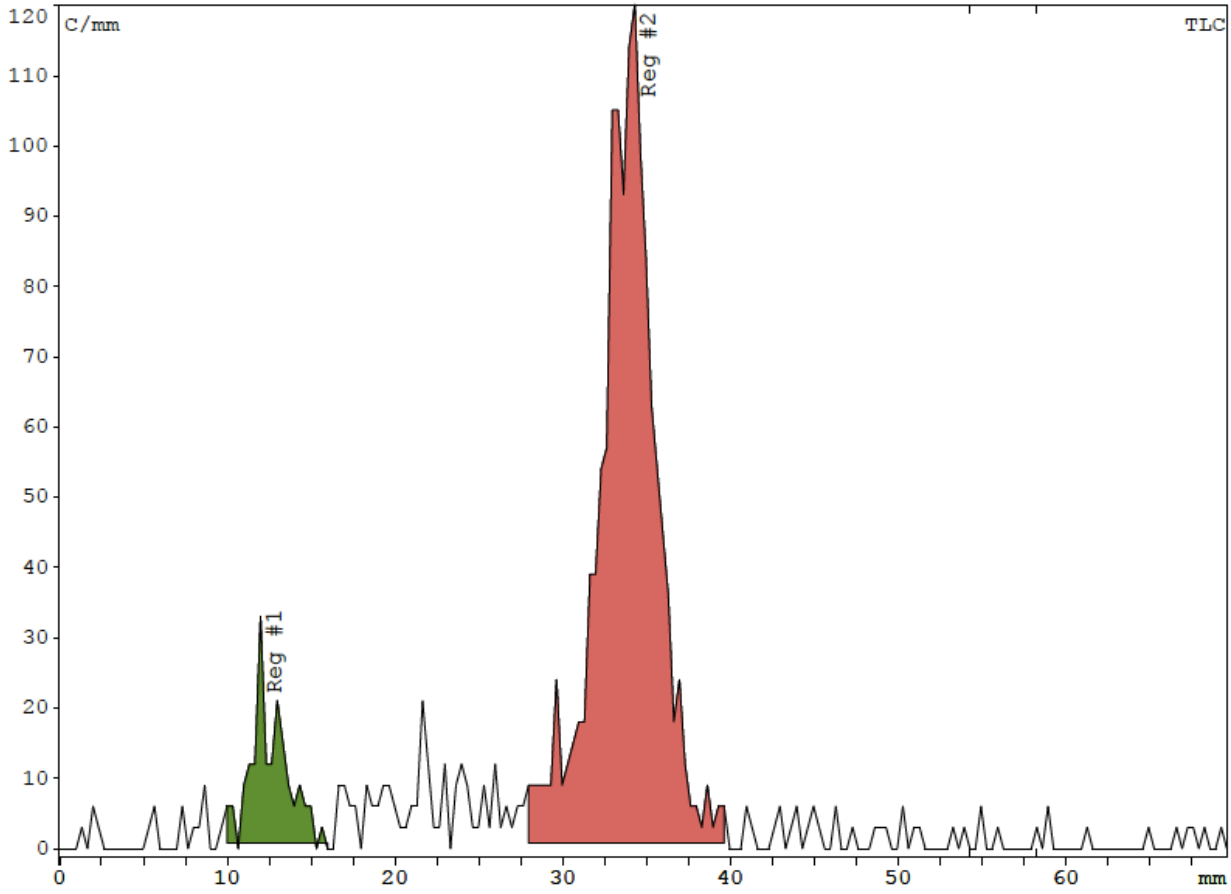
Standard procedure:



Integration TLC

Substance	R/F	%Total	Type	Area	%Area
		%		Counts	%
Reg #1	0,162	40,86	DD	713,6000	46,48
Reg #2	0,471	47,05	DD	821,8000	53,52
Sum in ROI				1535,4000	
Total area				1746,6000	
Area RF				1746,0000	
BKG1				1,80223	
Remainder RF				210,60	12,06
Remainder (Tot)				211,20	12,09

Standard procedure + 100 mol% PPh_3 + 1 min N_2



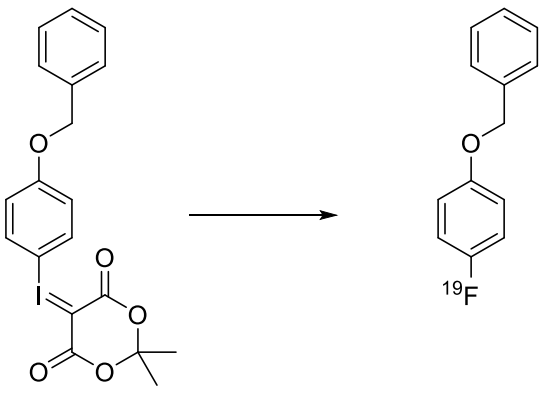
Integration TLC

Substance	R/F	%Total	Type	Area	%Area
		%		Counts	%
Reg #1	0,181	9,35	DD	54,5000	11,11
Reg #2	0,481	74,86	DD	436,2500	88,89
Sum in ROI				490,7500	
Total area				582,7500	
Area RF				583,5000	
BKG1				0,75093	
Remainder RF				92,75	15,90

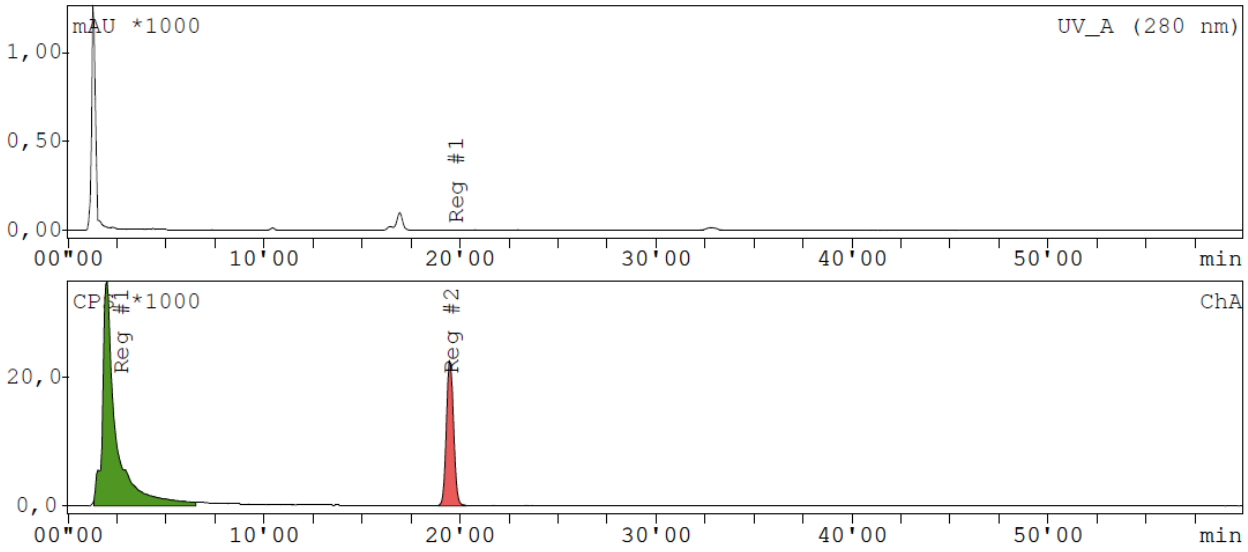
RCC

Entry	control	+PPh3	+N2	+PPh3, +N2
1	53,50	90,30	95,40	88,90
2	59,20	81,50	93,60	86,90
3	54,60	94,00		
4		92,60		

Entry	Conditions	Average RCC	Standard deviation	Repetitions
1	control	56	2	3
2	+PPh3	90	5	4
3	$+N_2$	95	1	2
4	+PPh3, +N2	88	1	2



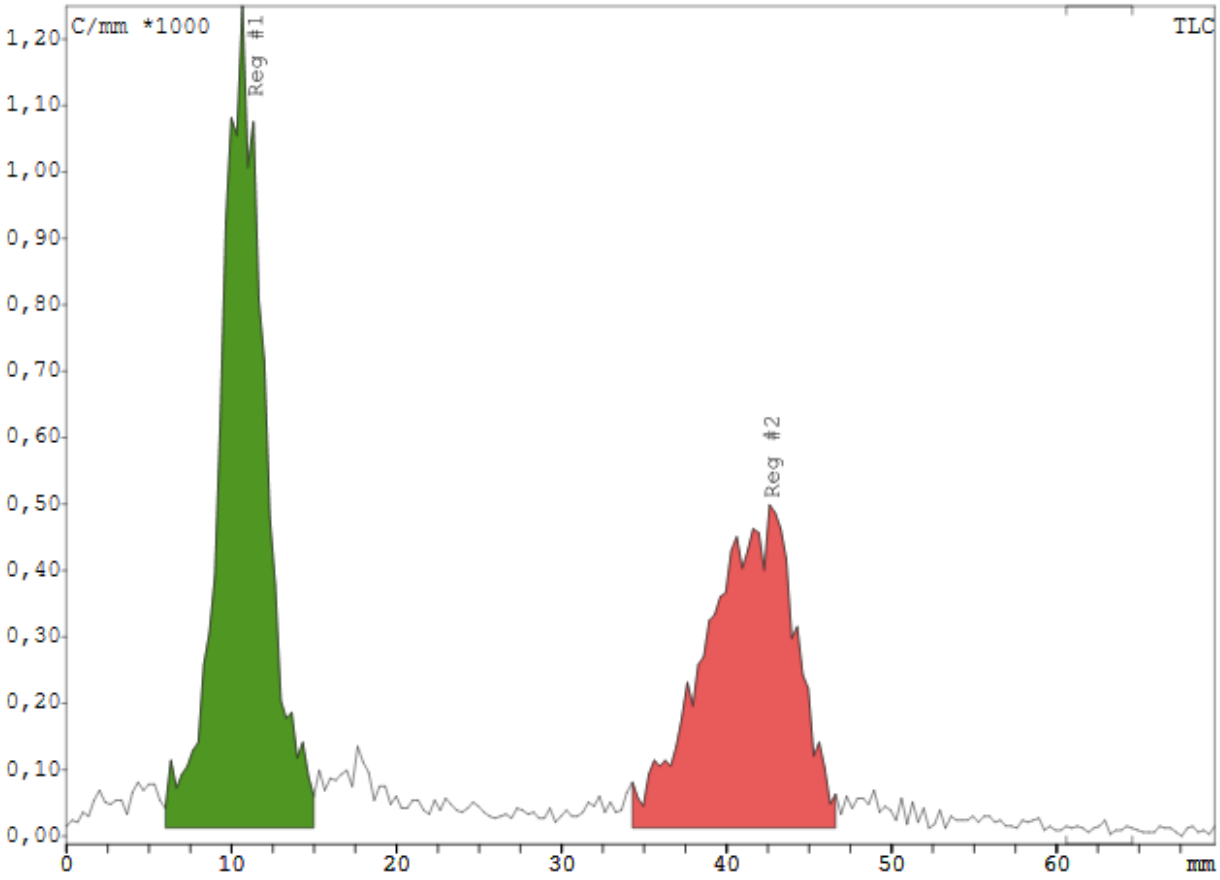
Standard procedure:



Integration ChA

Substance	R/T s	Type	Area Counts	%Area %
Reg #1	02'00	DD(M	1663504	74,63
Reg #2	19'28	DD(M	565502	25,37
Sum in ROI			2229005	100,00
Area (total)			2413841	
Ext. BKG			0,00 CPS	

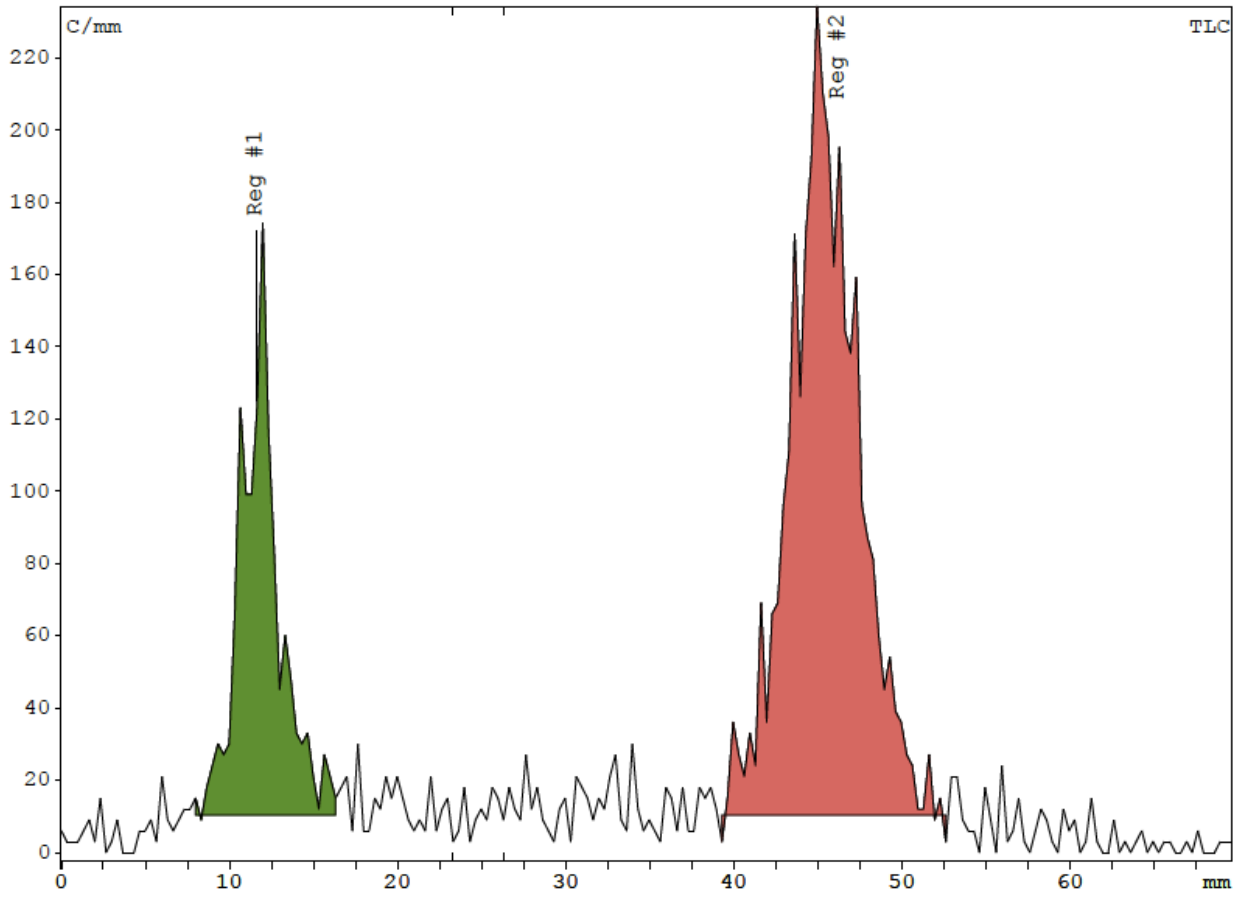
Standard procedure:



Integration TLC

Substance	R/F	%Total	Type	Area	%Area
		%		Counts	%
Reg #1	0,152	47,24	DD	3873,750	55,58
Reg #2	0,610	37,76	DD	3095,917	44,42
Sum in ROI				6969,667	
Total area				8199,583	
Area RF				8196,500	
BKG1				12,2652	
Remainder RF				1226,83	14,97
Remainder (Tot)				1229,92	15,00

Standard procedure + 100 mol% PPh_3 + 1 min N_2



Integration TLC

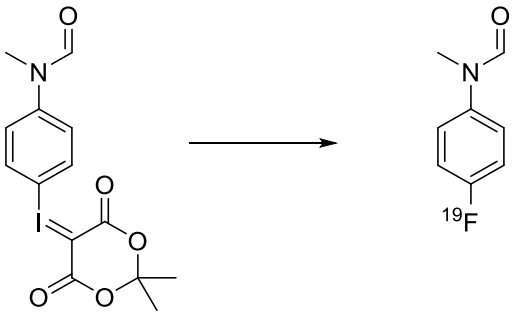
Substance	R/F	%Total	Type	Area	%Area
		%		Counts	%
Reg #1	0,162	28,90	DD	369,8889	27,56
Reg #2	0,643	75,95	DD	972,2222	72,44
Sum in ROI				1342,1111	
Total area				1280,1111	
Area RF				1277,6667	
BKG1				10,34616	

RCC

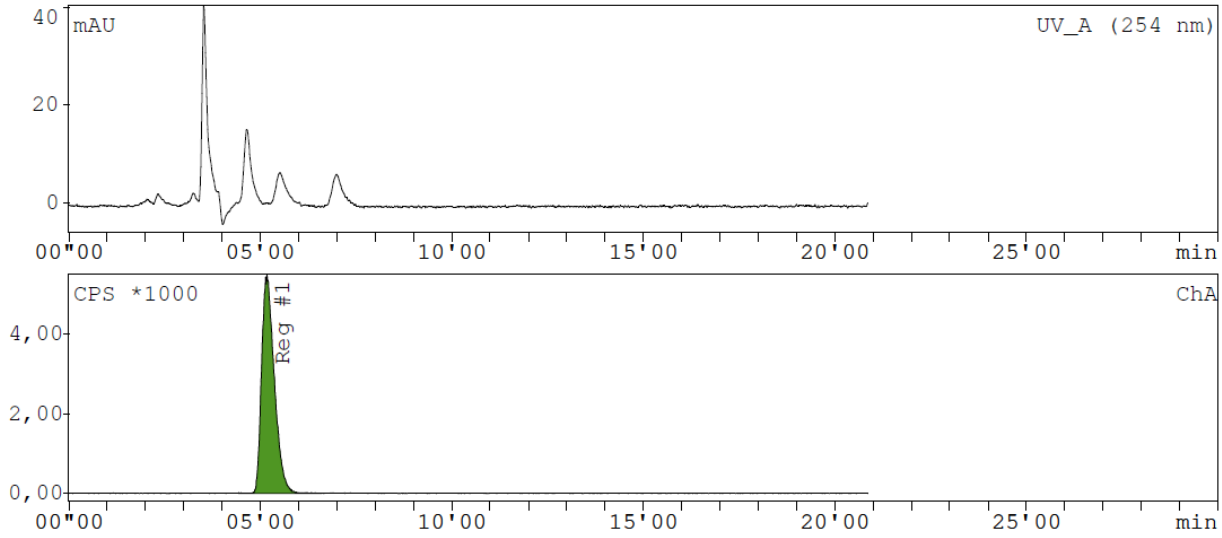
Entry	**control**	**+PPh3**	**+N2**	**+PPh3, +N2**
1	19	61	73,10	74,50
2	39	61	76,60	74,70
3	47	60		
4	50	65		
5	42	66		
6	43	71		
7	58	70		
8	52	69		
9	26	61		
10	44			
11	47			
12	58			
13	61			
14	50			
15	44			
16	47			
17	58			

RCC

Entry	**Conditions**	**Average RCC**	**Standard deviation**	**Repetitions**
1	control	46	11	17
2	+PPh3	65	4	9
3	$+N_2$	75	2	2
4	+PPh3, +N2	75	0	2



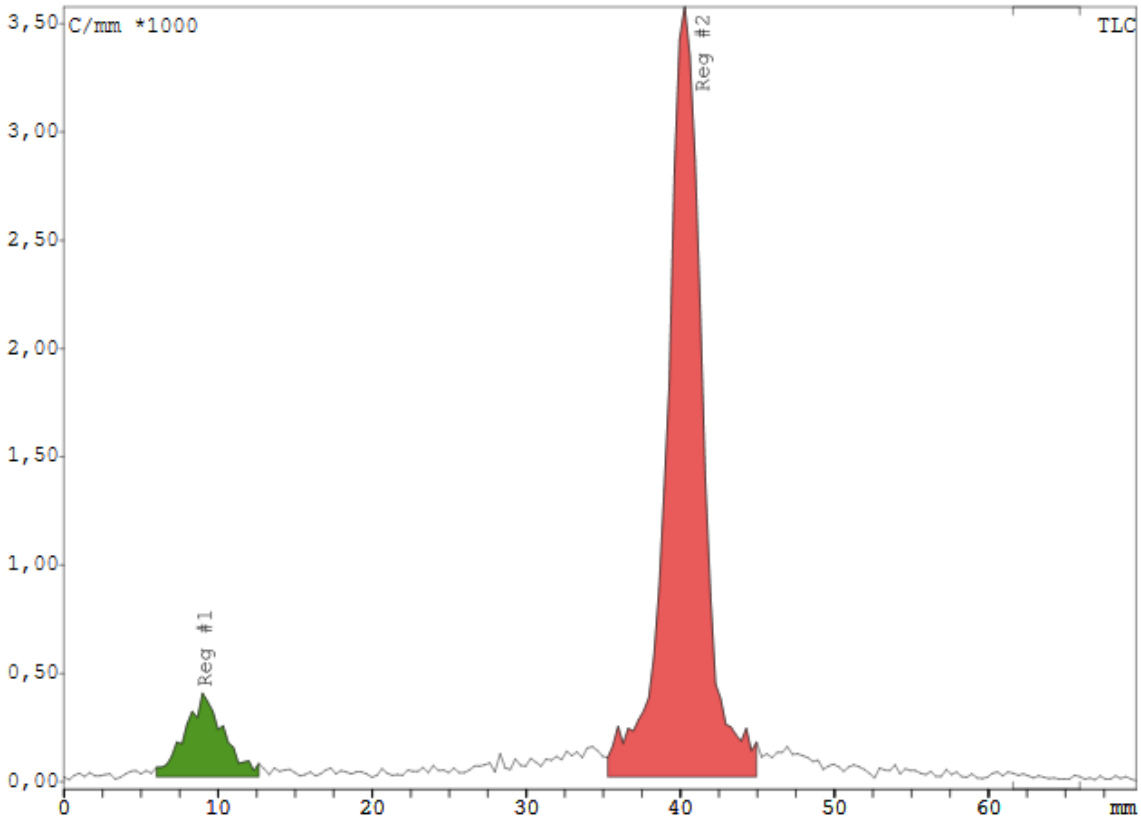
Standard procedure (purified on C18 cartridge)



Integration ChA

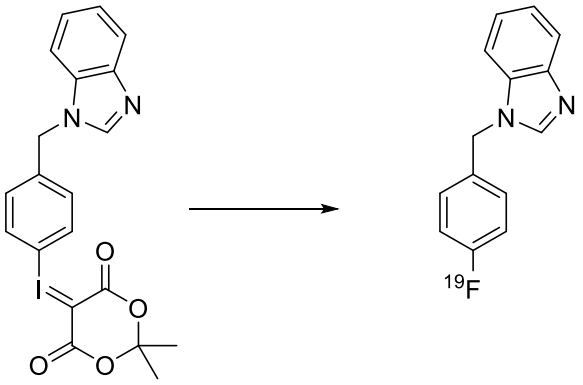
Substance	R/T s	Type	Area Counts	%Area %
Reg #1	05'11	DD(M	124764,4	100,00
Sum in ROI			124764,4	100,00
Area (total)			127532,4	
Ext. BKG			0,00 CPS	

Standard **procedure**

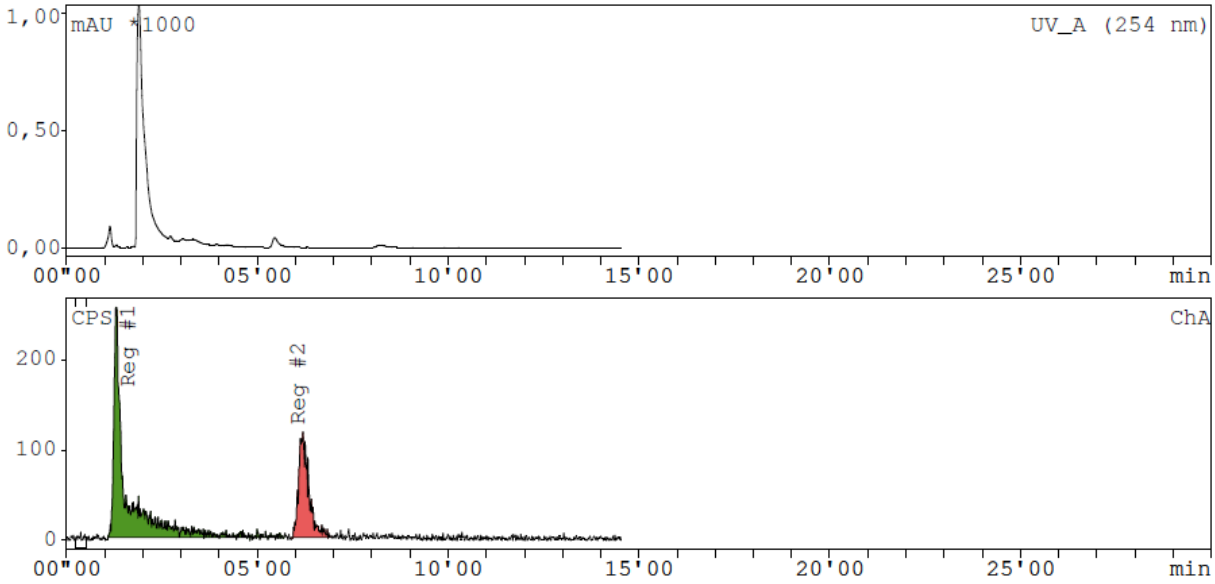


Integration TLC

Substance	R/F	%Total	Type	Area	%Area
		%		Counts	%
Reg #1	0,129	8,99	DD	1123,692	10,48
Reg #2	0,576	76,77	DD	9596,154	89,52
Sum in ROI				10719,846	
Total area				12499,385	
Area RF				12495,769	
BKG1				22,8745	
Remainder RF				1775,92	14,21
Remainder (Tot)				1779,54	14,24



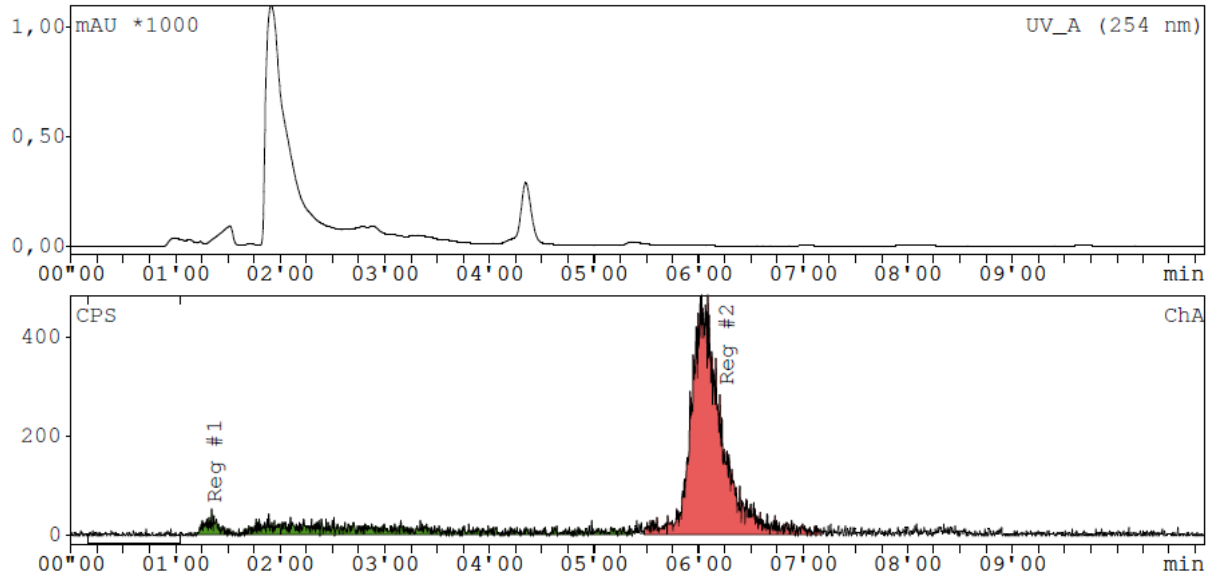
Standard procedure



Integration ChA

Substance	R/T s	Type	Area Counts	%Area %
Reg #1	01'18	DD(M	5040,091	70,40
Reg #2	06'12	DD(M	2119,065	29,60
Sum in ROI			7159,156	100,00
Area (total)			7011,274	
BKG1			2,9379	
Remainder			-147,88	-2,11

Standard procedure + 100 mol% PPh_3



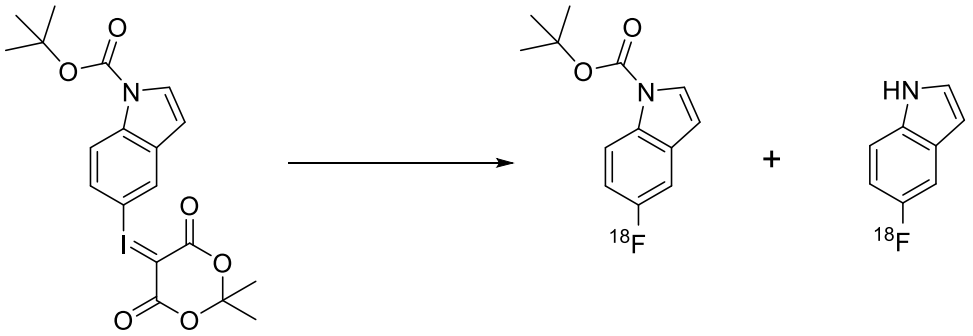
Integration ChA

Substance	R/T s	Type	Area Counts	%Area %
Reg #1	01'21	DD(M	2226,621	19,15
Reg #2	06'02	DD(M	9400,178	80,85
Sum in ROI			11626,799	100,00
Area (total)			12251,725	
BKG1			2,5424	
Remainder			624,93	5,10

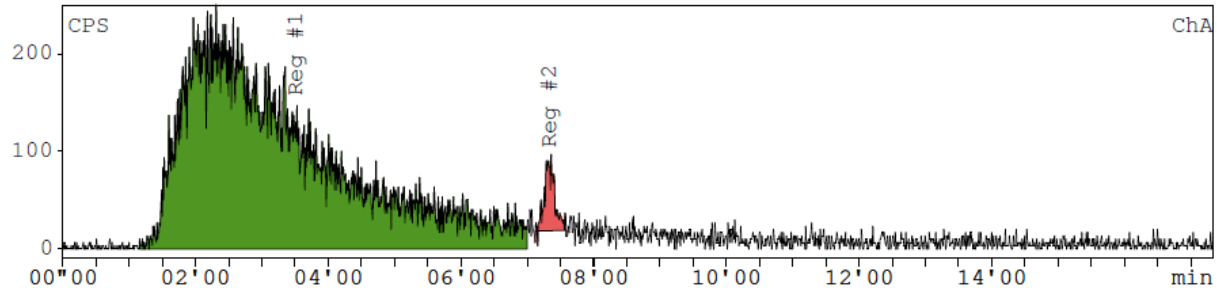
RCC

Entry	control	+PPh3	+N2	+PPh3, +N2
1	29,60	49,10	84,90	76,00
2	20,50	52,10	80,90	85,30

Entry	**Conditions**	**Average RCC**	**Standard deviation**	**Repetitions**
1	control	25	5	2
2	+PPh3	51	2	2
3	+PPh3, +N2	81	5	2
4	$+N_2$	83	2	2



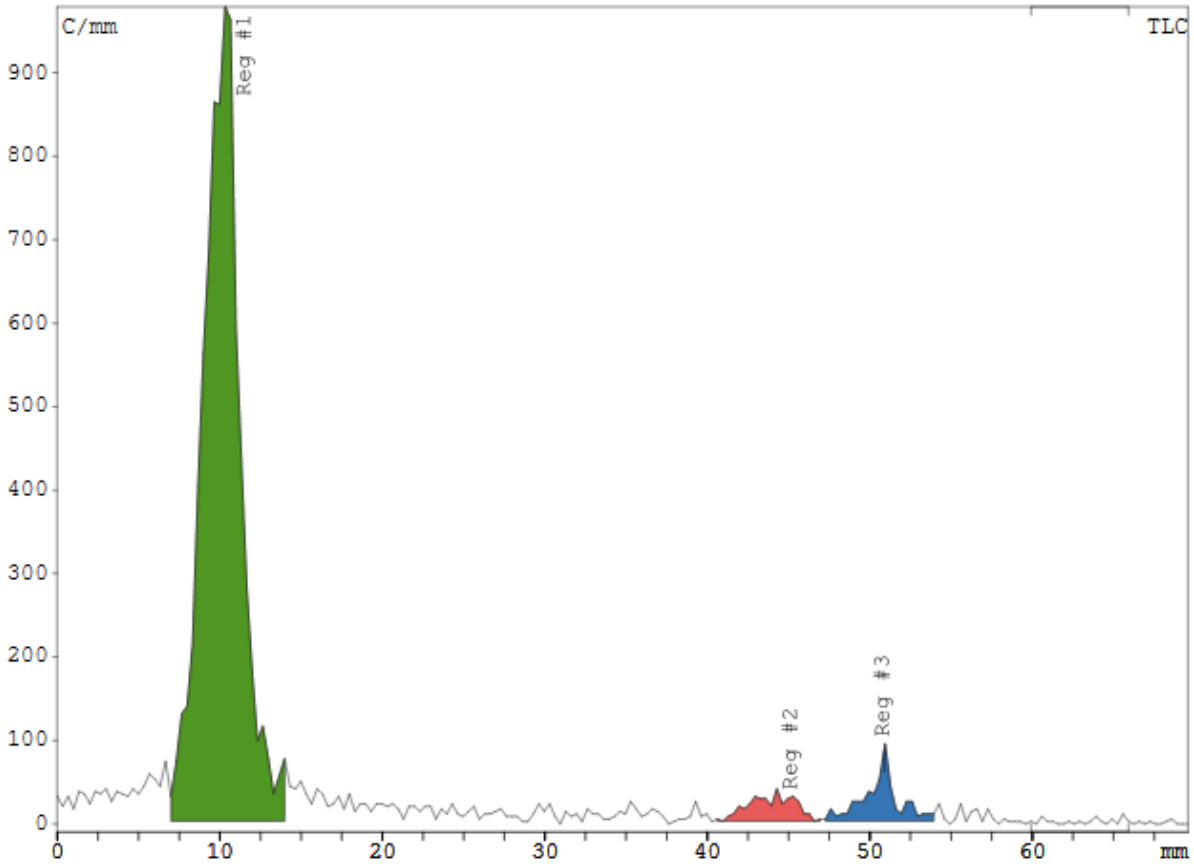
Standard procedure + 100 mol% PPh_3 + 1 min N_2



Integration ChA

Substance	R/T s	Type	Area Counts	%Area %
Reg #1	02'18	DD(M	30136,33	97,48
Reg #2	07'19	BB(M	778,74	2,52
Sum in ROI			30915,08	100,00
Area (total)			36803,55	
Ext. BKG			0,00 CPS	

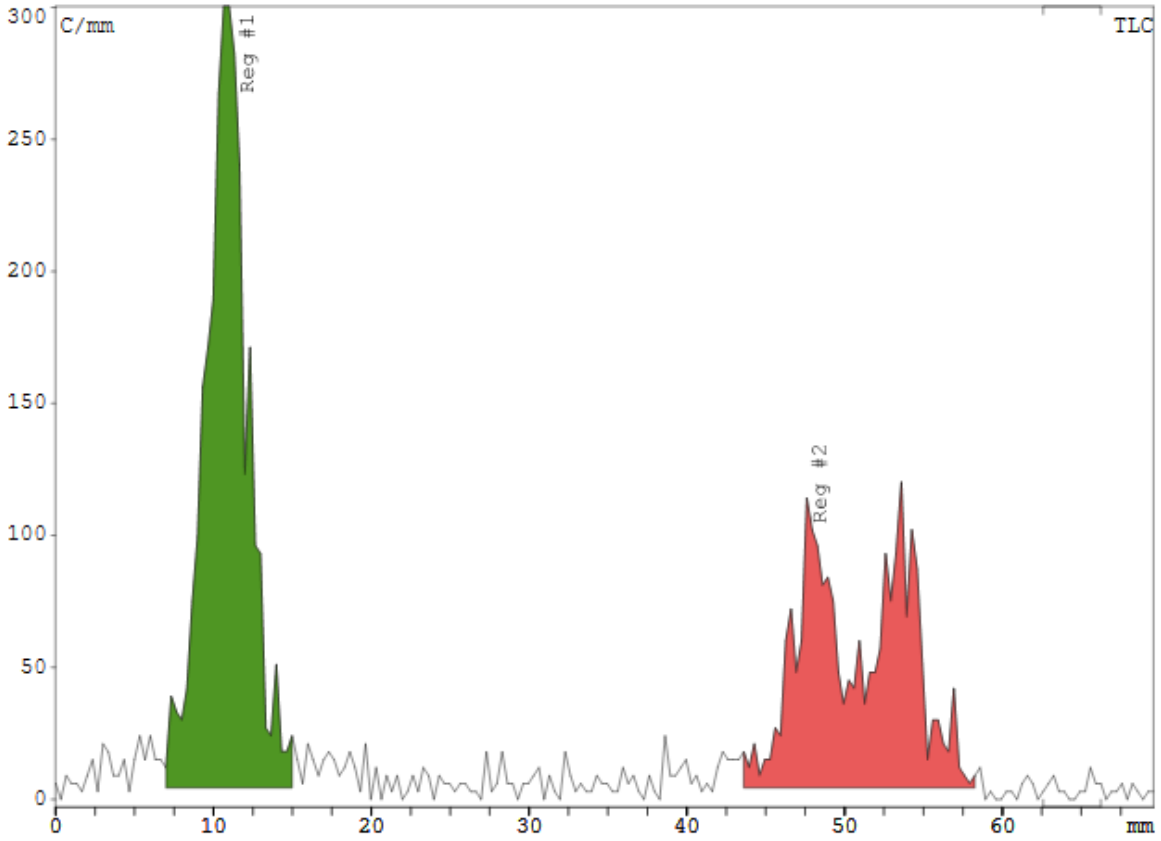
Standard procedure



Integration TLC

Substance	R/F	%Total	Type	Area	%Area
		%		Counts	%
Reg #1	0,143	73,75	DD	2577,833	90,72
Reg #2	0,643	3,15	DD	109,944	3,87
Reg #3	0,724	4,40	DD	153,889	5,42
Sum in ROI				2841,667	
Total area				3495,389	
Area RF				3494,333	
BKG1				3,1706	
Remainder RF				652,67	18,68
Remainder (Tot)				653,72	18,70

Standard procedure + 100 mol% PPh_3 + 1 min N_2



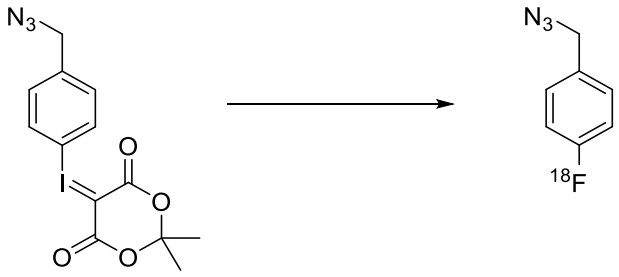
Integration TLC

Substance	R/F	%Total	Type	Area	%Area
		%		Counts	%
Reg #1	0,157	52,44	DD	917,0909	57,49
Reg #2	0,690	38,77	DD	678,0000	42,51
Sum in ROI				1595,0909	
Total area				1749,0000	
Area RF				1748,5455	
BKG1				4,36905	
Remainder RF				153,45	8,78
Remainder (Tot)				153,91	8,80

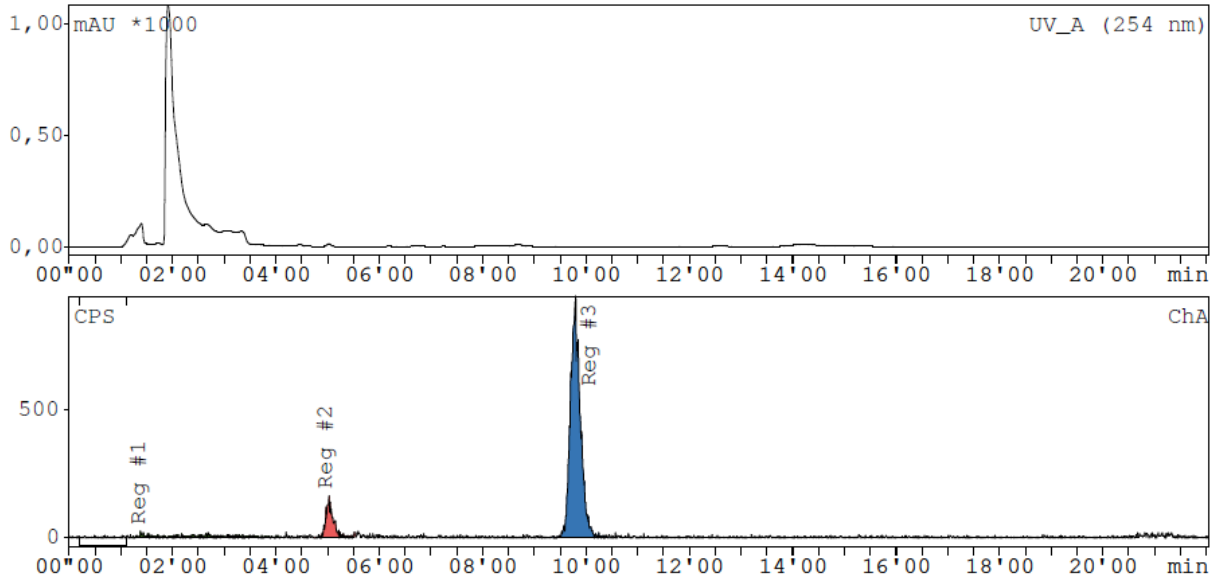
	-Boc	+Boc	RCC	ratio boc	+boc/-
control	1,9	3,2	5,1	1,7	
control	3,9	5,4	9,3	1,4	

+PPh3	10,8	11,5	22,3	1,1
+PPh3	12,9	13,1	26	1,0
+N2	20,4	13,8	34,2	0,7
+N2	23,1	17,8	40,9	0,8
+N2	18	19,3	37,3	1,1
+N2	18,1	16	34,1	0,9
+PPh3, +N2	16,6	22,3	38,9	1,3
+PPh3, +N2	14,3	18,1	32,4	1,3
+PPh3, +N2	20,4	21,6	42	1,1

Entry	**RCC control**	**+PPh3**	**+N2**	**+PPh3, +N2Repetitions**
1	control	7	2	2
2	+PPh3	24	2	2
3	$+N_2$	37	3	4
4	+PPh3, +N2	38	4	3



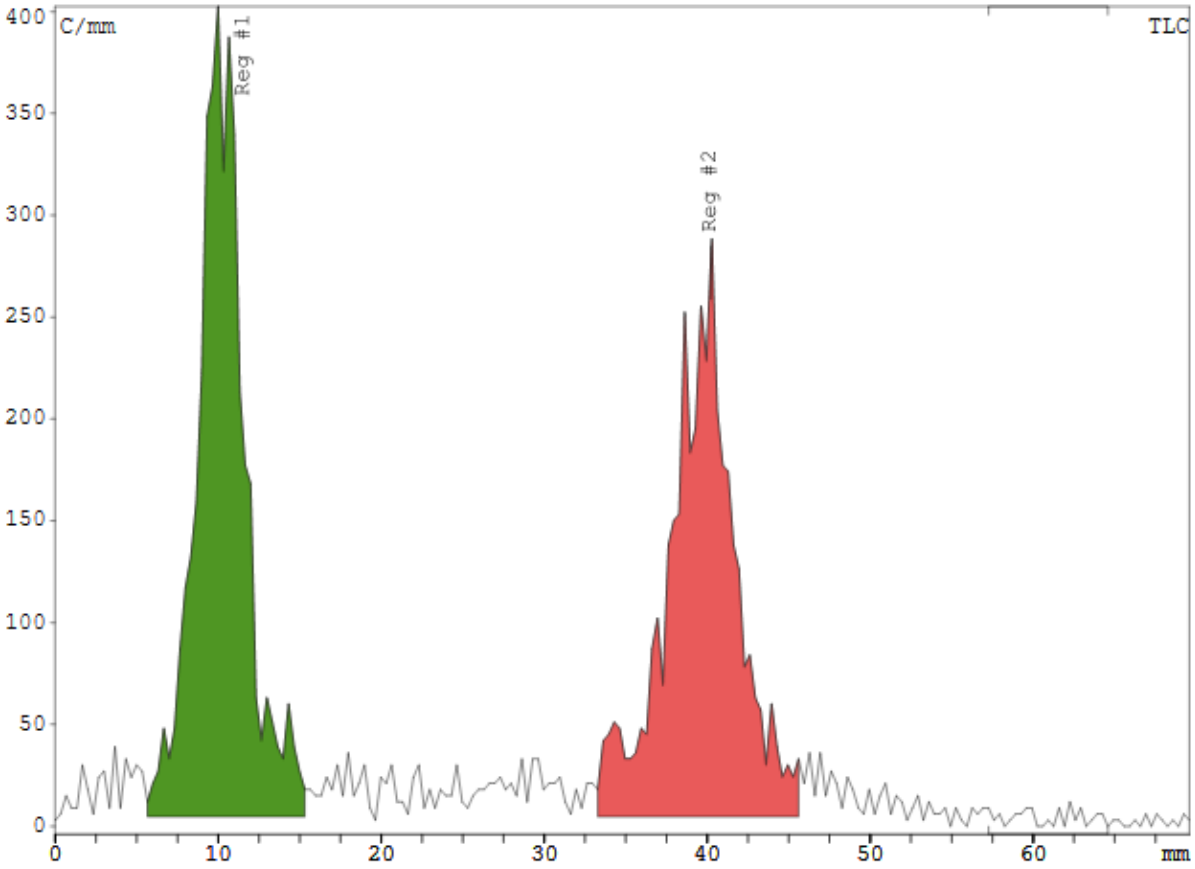
Standard procedure + 100 mol% PPh_3



Integration ChA

Substance	R/T s	Type	Area Counts	%Area %
Reg #1	01'23	DD(M	532,24	3,72
Reg #2	05'01	DD(M	1480,87	10,35
Reg #3	09'47	DD(M	12291,48	85,93
Sum in ROI			14304,59	100,00
Area (total)			15012,73	
BKG1			2,295	
Remainder			708,14	4,72

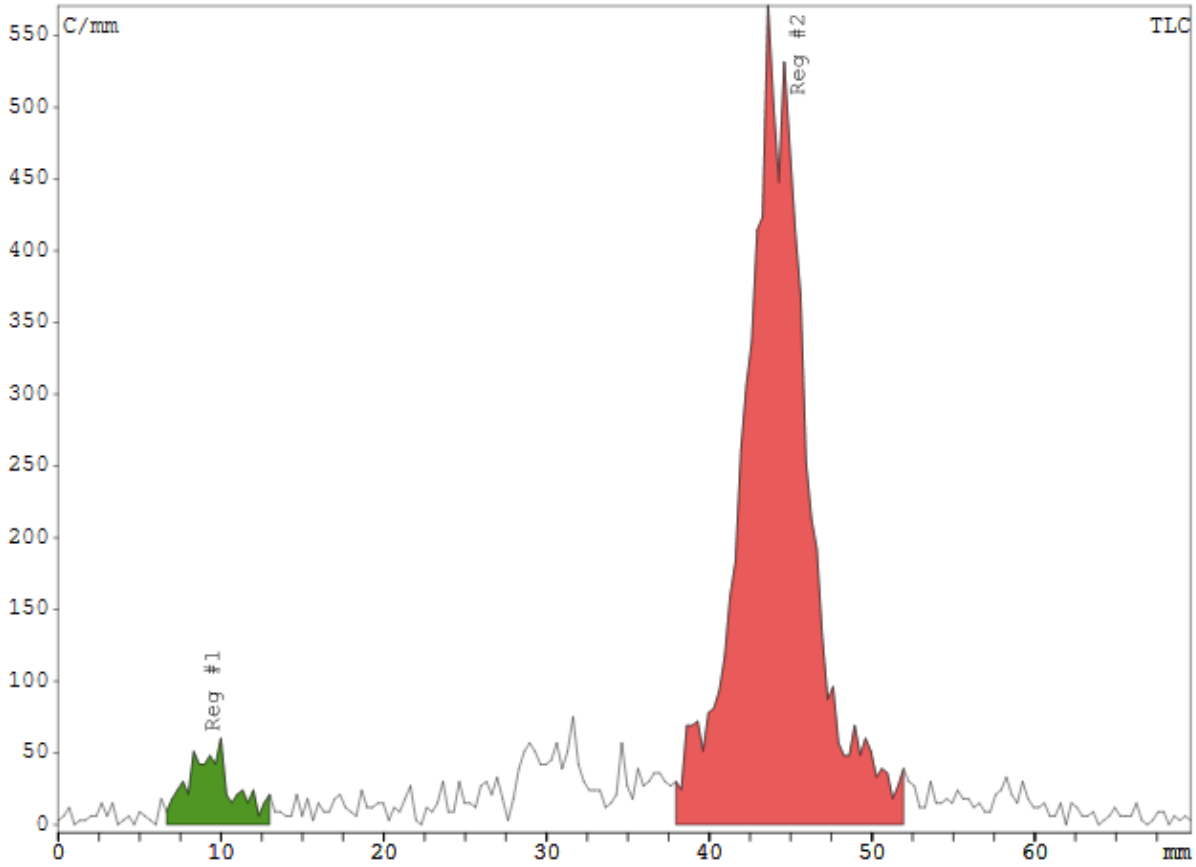
Standard procedure



Integration TLC

Substance	R/F	%Total	Type	Area	%Area
		%		Counts	%
Reg #1	0,143	44,35	DD	1302,182	51,80
Reg #2	0,571	41,27	DD	1211,818	48,20
Sum in ROI				2514,000	
Total area				2936,000	
Area RF				2936,455	
BKG1				4,6421	
Remainder RF				422,45	14,39
Remainder (Tot)				422,00	14,37

Standard procedure + 100 mol% PPh_3



Integration TLC

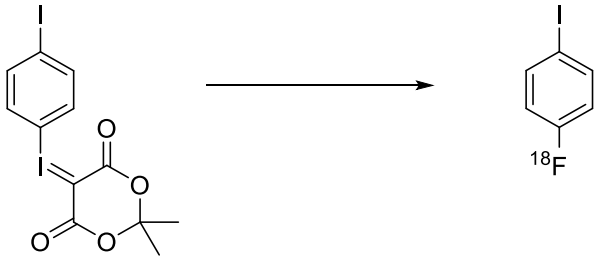
Substance	R/F	%Total	Type	Area	%Area
		%		Counts	%
Reg #1	0,133	4,97	DD	176,000	6,52
Reg #2	0,633	71,25	DD	2525,000	93,48
Sum in ROI				2701,000	
Total area				3544,000	
Area RF				3546,000	

RCC

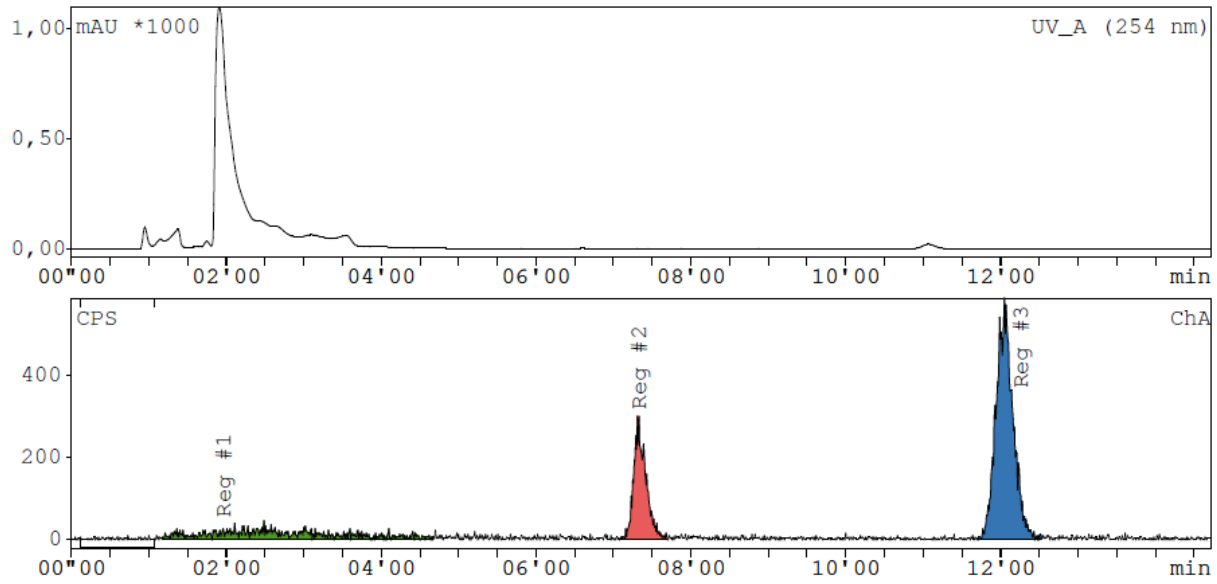
Entry	**control**	**+N2**
1	18,20	89,80
2	48,20	93,50

Entry	**RCC Conditions**	**Average**	**Standard deviation**	**Repetitions**

1	control	33	15	2
2	+N_2	92	2	2



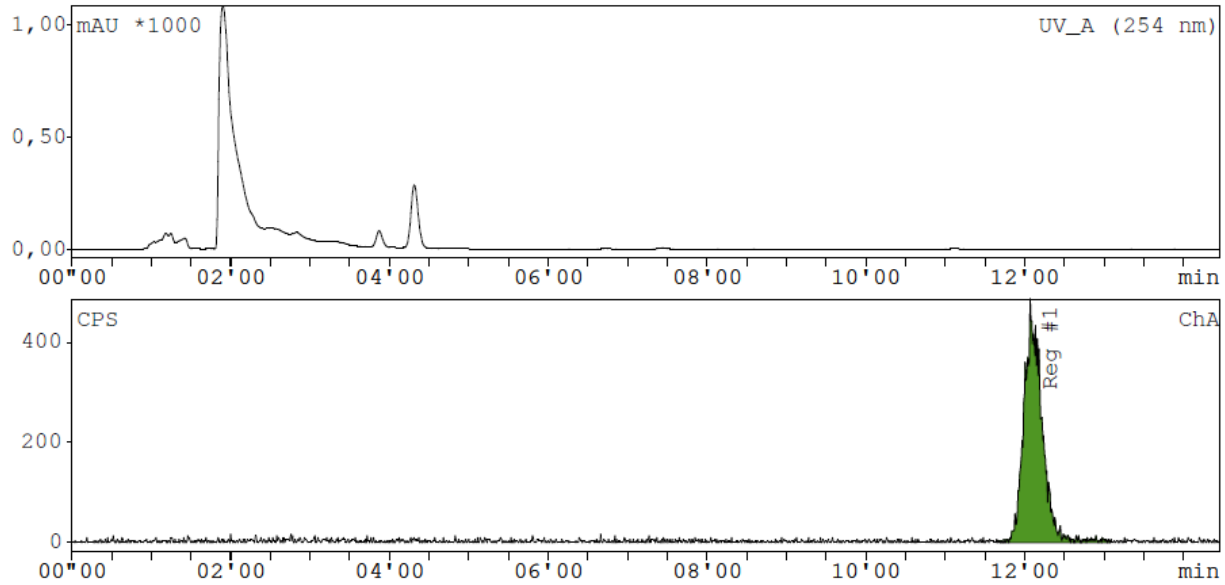
Standard procedure



Integration ChA

Substance	R/T s	Type	Area Counts	%Area %
Reg #1	01'57	DD(M	2184,057	15,67
Reg #2	07'19	DD(M	3049,020	21,88
Reg #3	12'03	DD(M	8704,926	62,45
Sum in ROI			13938,004	100,00
Area (total)			14892,751	
BKG1			1,7544	
Remainder			954,75	6,41

Standard procedure + 100 mol% PPh_3 + 1 min N_2

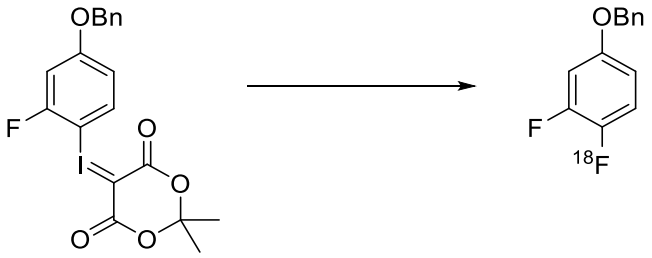


Integration ChA

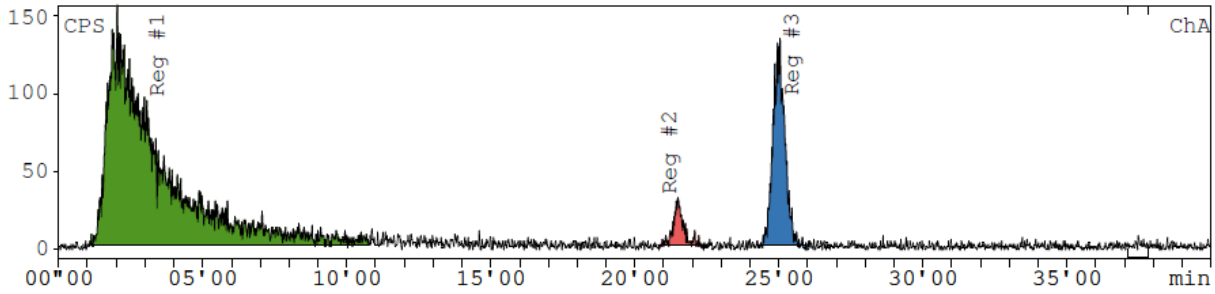
Substance	R/T s	Type	Area Counts	%Area %
Reg #1	12'06	DD(M	7318,541	100,00
Sum in ROI			7318,541	100,00
Area (total)			9409,552	
Ext. BKG			0,00 CPS	

	4-Fluoro-1-iodobenzene	Fluorobenzene	RCC	ratio
control	62,50	21,88	84,38	0,74
control	62,40	23,10	85,50	0,73
+PPh3	84,40	5,70	90,10	0,94
+PPh3	81,60	4,60	86,20	0,95
+N2	98,70	1,30	100,00	0,99
+N2	89,70	1,00	90,70	0,99
+PPh3, +N2	100,00	0,00	100,00	1,00
+PPh3, +N2	100,00	0,00	100,00	1,00

Entry	RCC control	+PPh3	+N2	+PPh3, +N2	Repetitions
1	control	85	1	1:3	2
2	+PPh3	88	2	1:19	2
3	+N_2	95	5	1:99	2
4	+PPh3, +N2	100	0	0:1	2



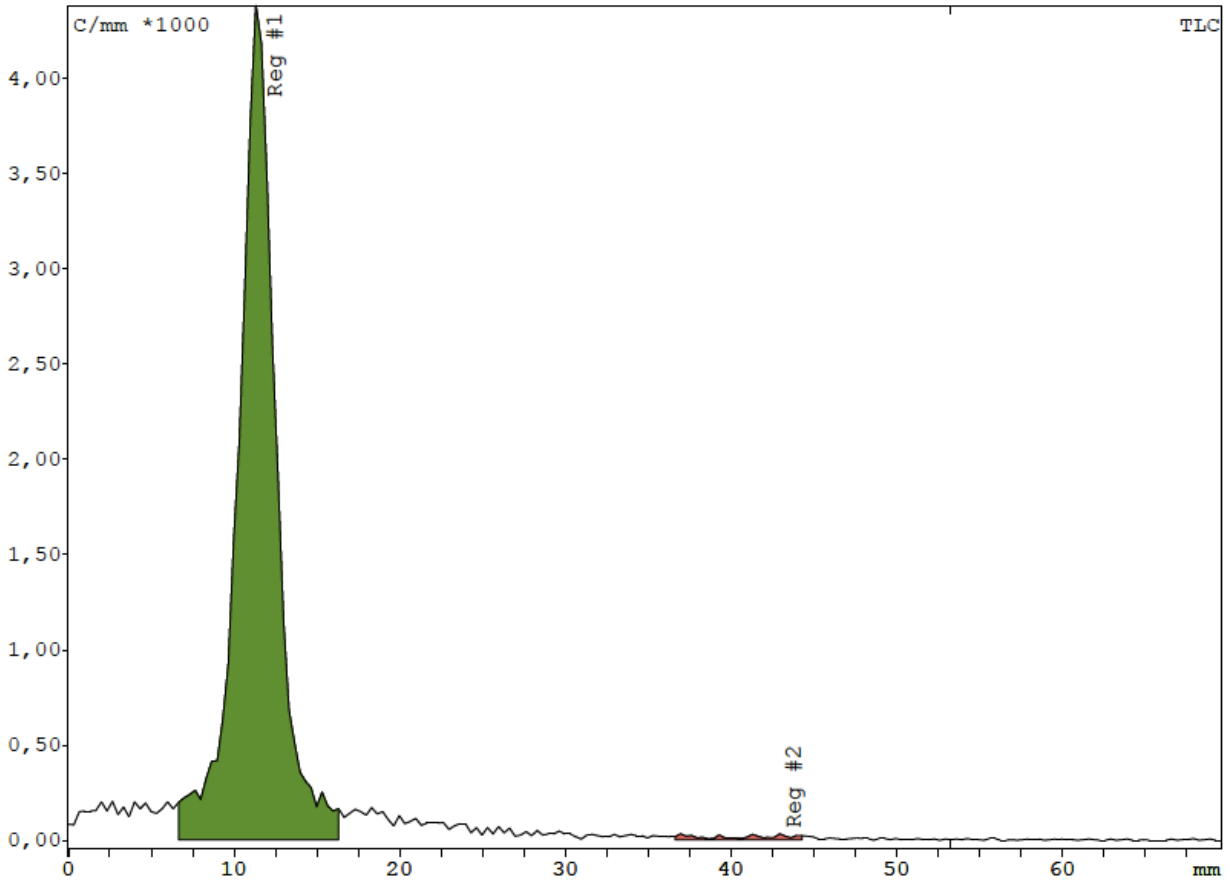
Standard procedure + 100 mol% PPh_3 + 1 min N_2



Integration ChA

Substance	R/T s	Type	Area Counts	%Area %
Reg #1	02'03	DD(M	16672,68	79,86
Reg #2	21'29	DD(M	600,68	2,88
Reg #3	25'00	DD(M	3603,19	17,26
Sum in ROI			20876,56	100,00
Area (total)			20537,83	
BKG1			3,035	
Remainder			-338,73	-1,65

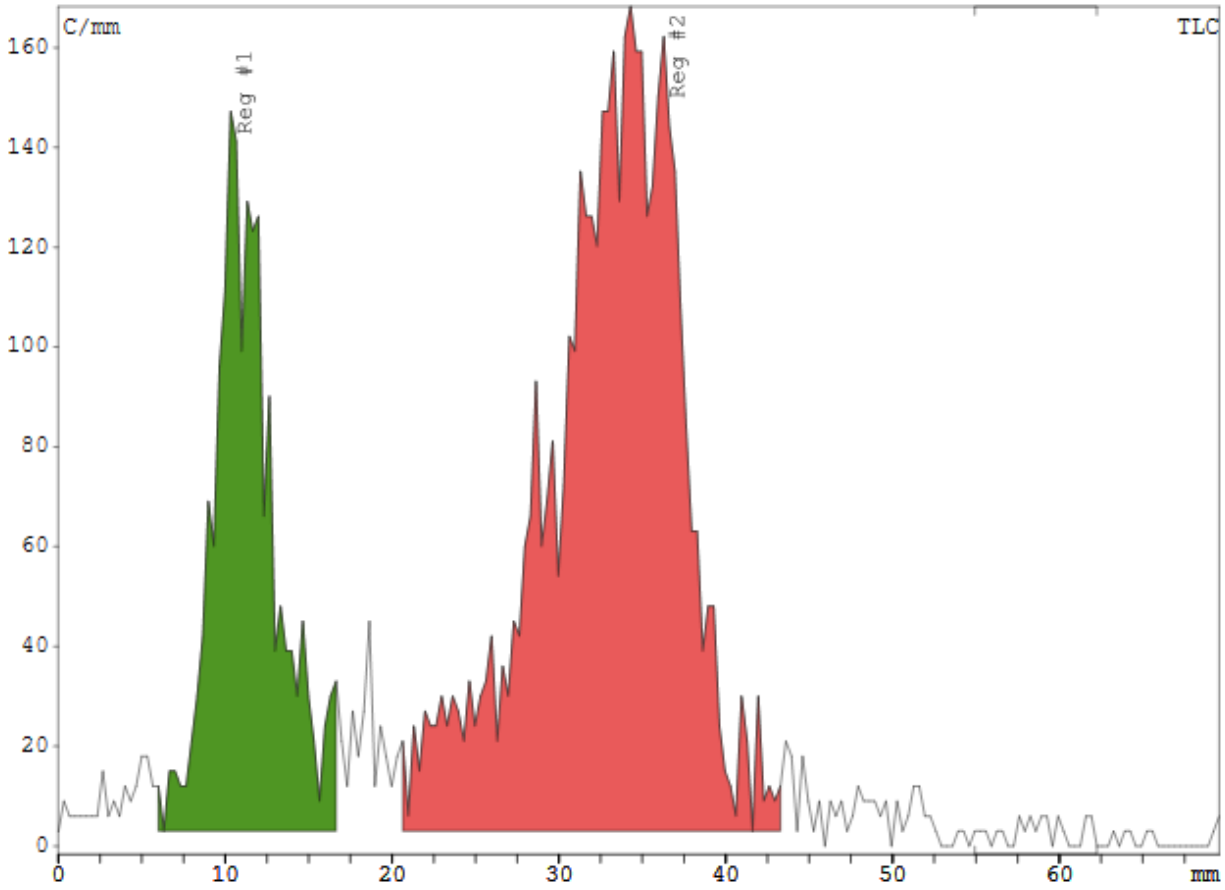
Standard procedure:



Integration TLC

Substance	R/F	%Total	Type	Area	%Area
		%		Counts	%
Reg #1	0,162	82,77	DD	11568,41	99,04
Reg #2	0,624	0,81	DD	112,53	0,96
Sum in ROI				11680,94	
Total area				13976,73	
Area RF				13975,71	
BKG1				3,065	

Standard procedure + 100 mol% PPh_3 + 1 min N_2



Integration TLC

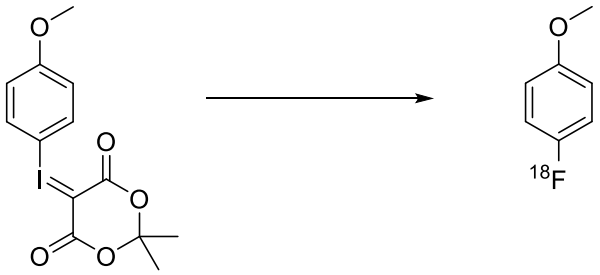
Substance	R/F	%Total	Type	Area	%Area
		%		Counts	%
Reg #1	0,157	25,88	DD	559,000	27,73
Reg #2	0,490	67,45	DD	1457,000	72,27
Sum in ROI				2016,000	
Total area				2160,000	
Area RF				2160,000	
BKG1				3,0037	
Remainder RF				144,00	6,67
Remainder (Tot)				144,00	6,67

RCC

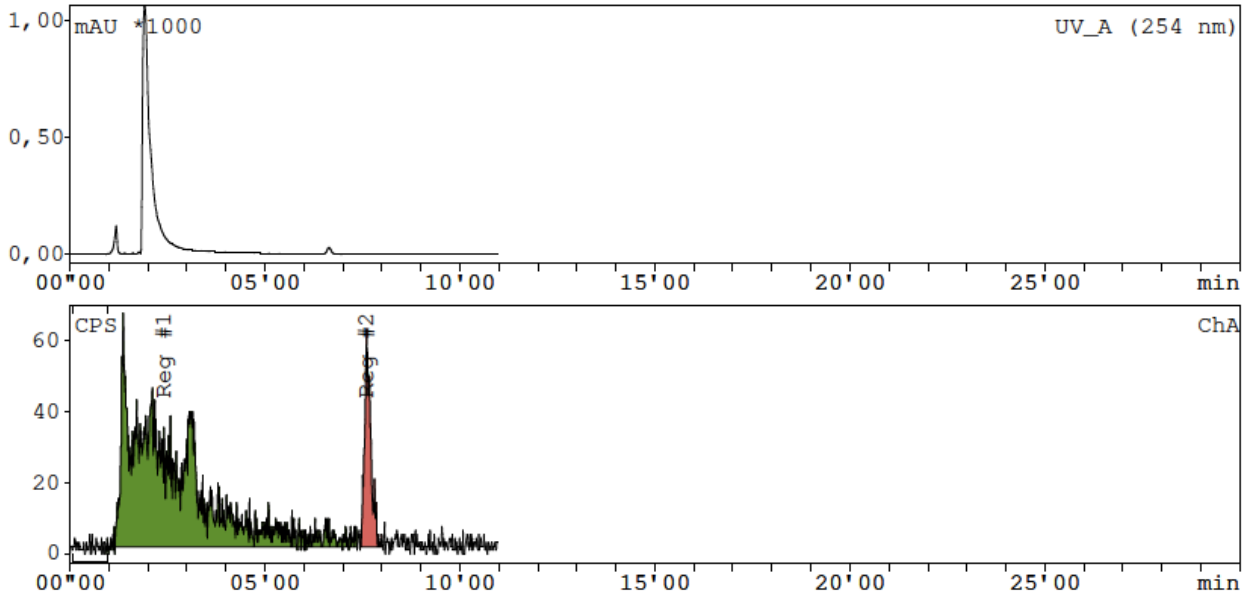
Entry	**control**	**+PPh3**	**+N2**	**+PPh3, +N2**
1	traces	11,10	70,60	48,90

2		traces	25,10	52,80	72,40
3		traces	9,60	50,60	64,20
4		traces	21,10		

Entry	**RCC Conditions**	**Average RCC**	**Standard deviation**	**Product:Byproduct**	**Repetitions**
1	control	traces	NA	NA	4
2	+PPh3	17	7	1:6	4
3	+N_2	58	9	1:11	3
4	+PPh3, +N2	62	10	1:11	3



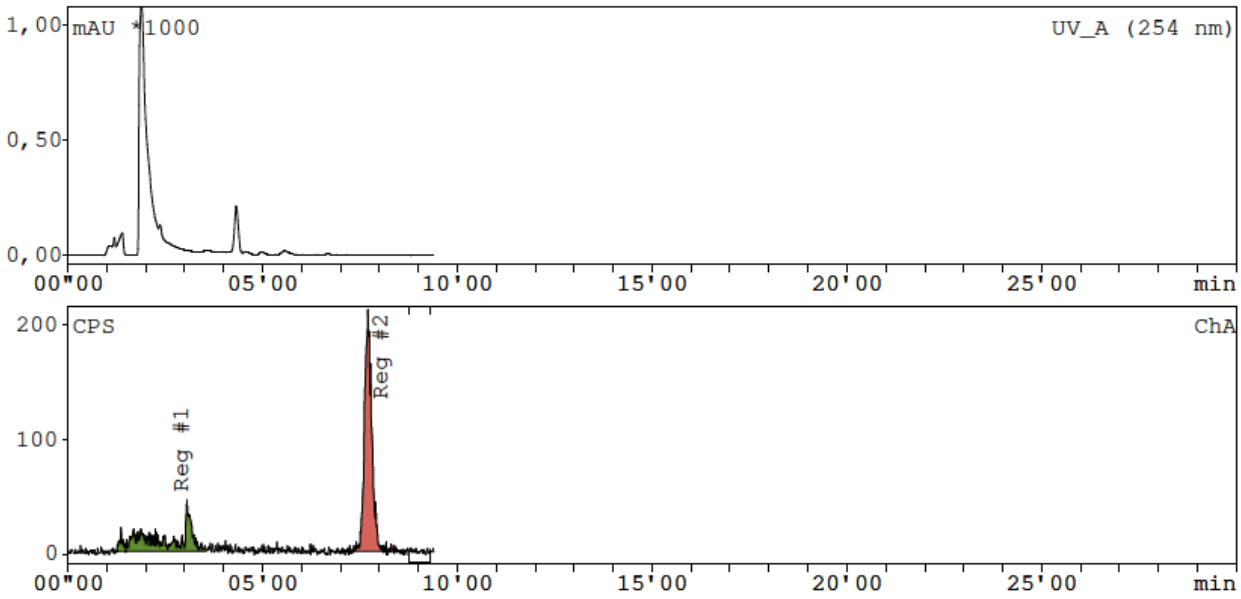
Standard procedure:



Integration ChA

Substance	R/T s	Type	Area Counts	%Area %
Reg #1	01'22	DD(M	4701,648	87,97
Reg #2	07'37	DD(M	643,155	12,03
Sum in ROI			5344,803	100,00
Area (total)			5490,187	
BKG1			2,0599	

Standard procedure + 100 mol% PPh_3 + 1 min N_2



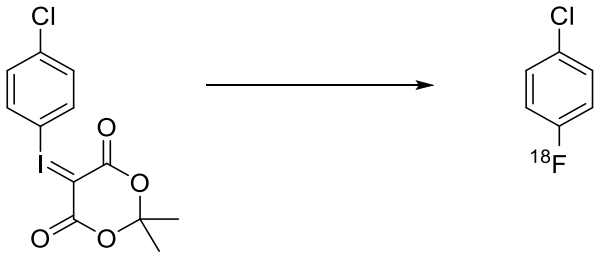
Integration ChA

Substance	R/T s	Type	Area Counts	%Area %
Reg #1	03'04	DD(M	1367,476	34,00
Reg #2	07'42	DD(M	2655,095	66,00
Sum in ROI			4022,571	100,00
Area (total)			4197,349	
BKG1			2,8661	

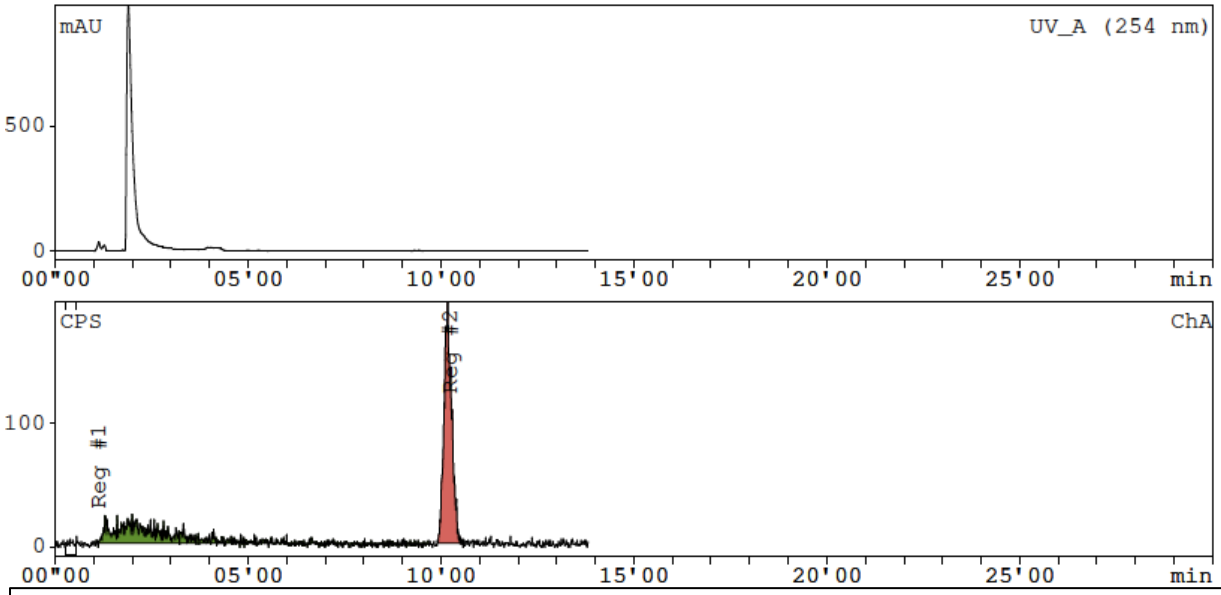
RCC

Entry	**control**	**+PPh3**	**+N2**	**+PPh3, +N2**
1	12	43,6	69,2	55
2	9,7	40,4	69,3	60,9
3			61,4	

Entry	Conditions	Average RCC	Standard deviation	Repetitions
1	control	11	1	2
2	+PPh3	42	2	2
3	+N_2	67	4	3
4	+PPh3, +N2	58	3	2



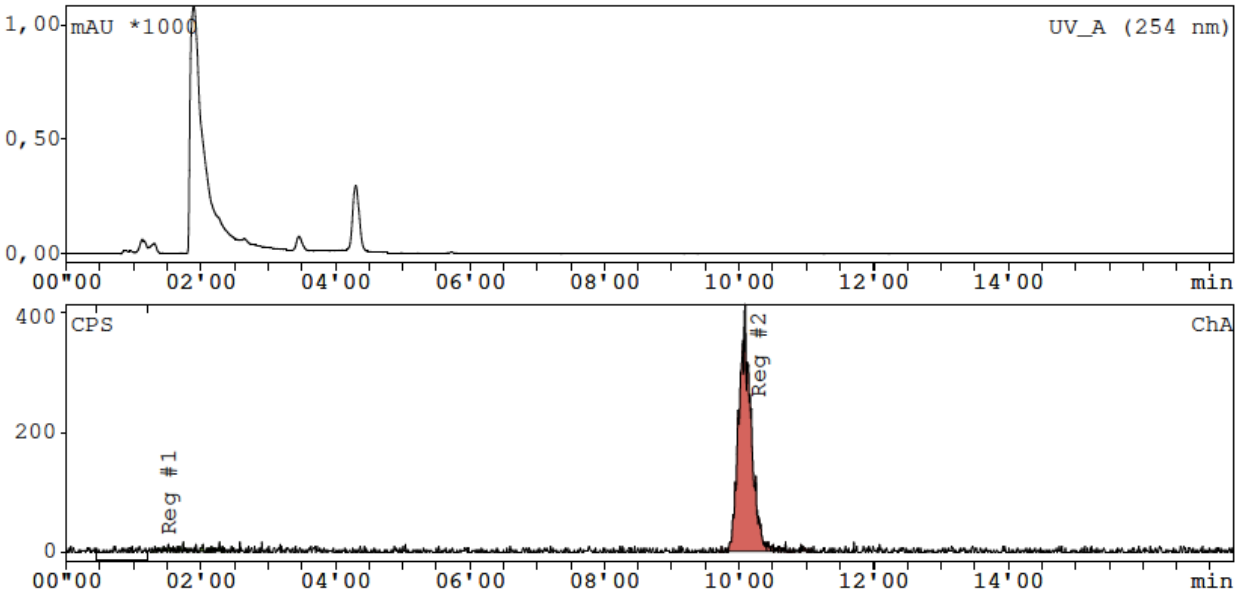
Standard procedure:



Integration ChA

Substance	R/T s	Type	Area Counts	%Area %
Reg #1	01'18	DD(M	1402,042	35,20
Reg #2	10'10	DD(M	2581,551	64,80
Sum in ROI			3983,593	100,00
Area (total)			3810,593	
BKG1			3,3333	

Standard procedure + 100 mol% PPh_3 + 1 min N_2



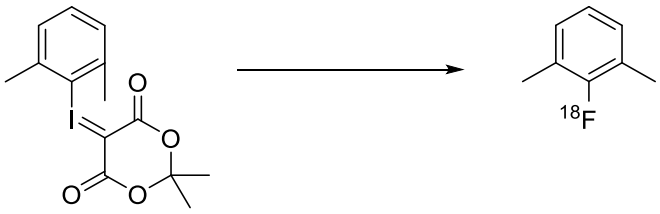
Integration ChA

Substance	R/T s	Type	Area Counts	%Area %
Reg #1	01'31	DD(M	142,599	2,79
Reg #2	10'05	DD(M	4968,513	97,21
Sum in ROI			5111,112	100,00
Area (total)			5211,178	
BKG1			2,2944	

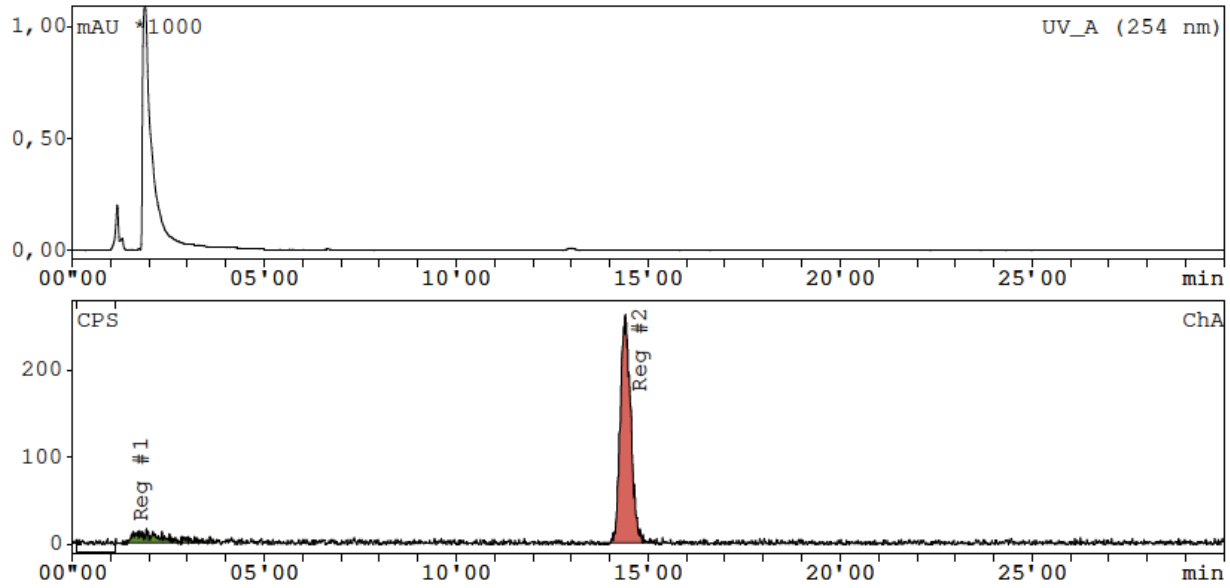
RCC

Entry	control	+PPh3	+N2	+PPh3, +N2
1	35,20	54,60	96,30	97,20
2	13,60	56,80	95,80	94,80

Entry	Conditions	Average RCC	Standard deviation	Repetitions
1	control	24	11	2
2	+PPh3	56	1	2
3	$+N_2$	96	0	2
4	+PPh3, +N2	96	1	2



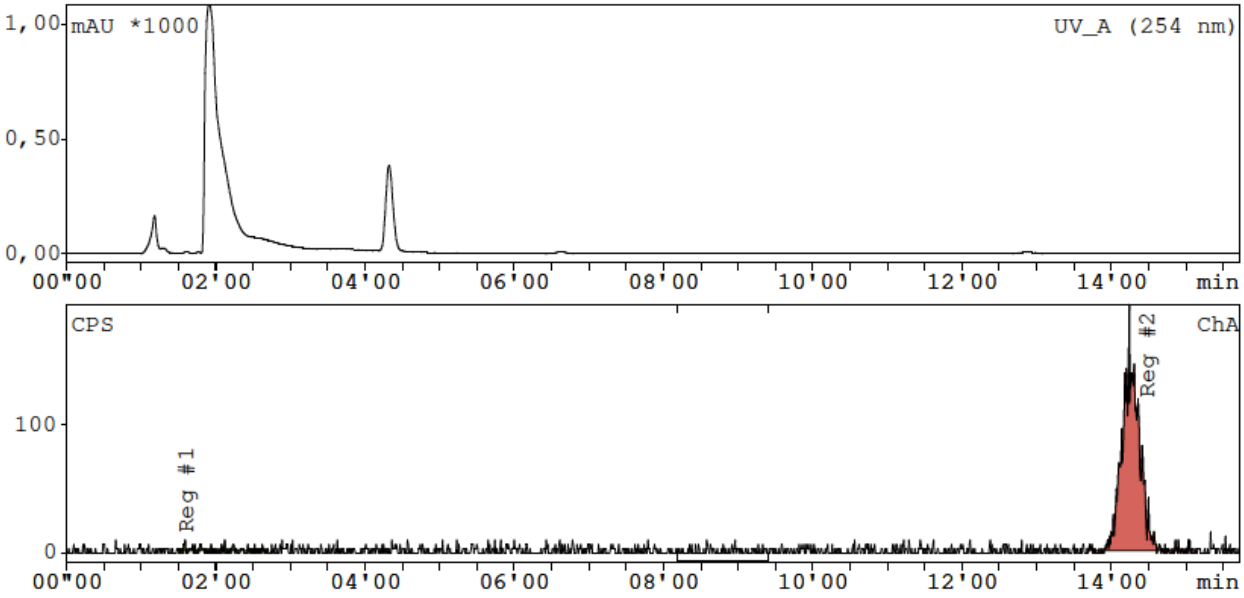
Standard procedure:



Integration ChA

Substance	R/T s	Type	Area Counts	%Area %
Reg #1	01'56	DD(M	630,061	11,53
Reg #2	14'25	DD(M	4832,621	88,47
Sum in ROI			5462,681	100,00
Area (total)			5504,290	
BKG1			2,1896	

Standard procedure + 100 mol% PPh_3 + 1 min N_2



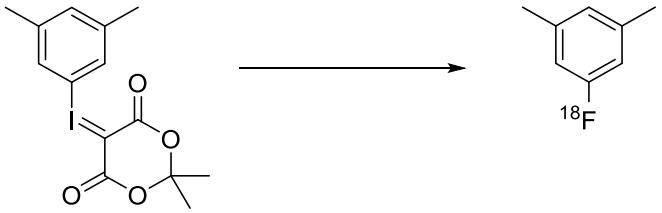
Integration ChA

Substance	R/T s	Type	Area Counts	%Area %
Reg #1	01'35	DD(M	20,430	0,78
Reg #2	14'18	DD(M	2603,363	99,22
Sum in ROI			2623,793	100,00
Area (total)			2701,962	
BKG1			1,8989	

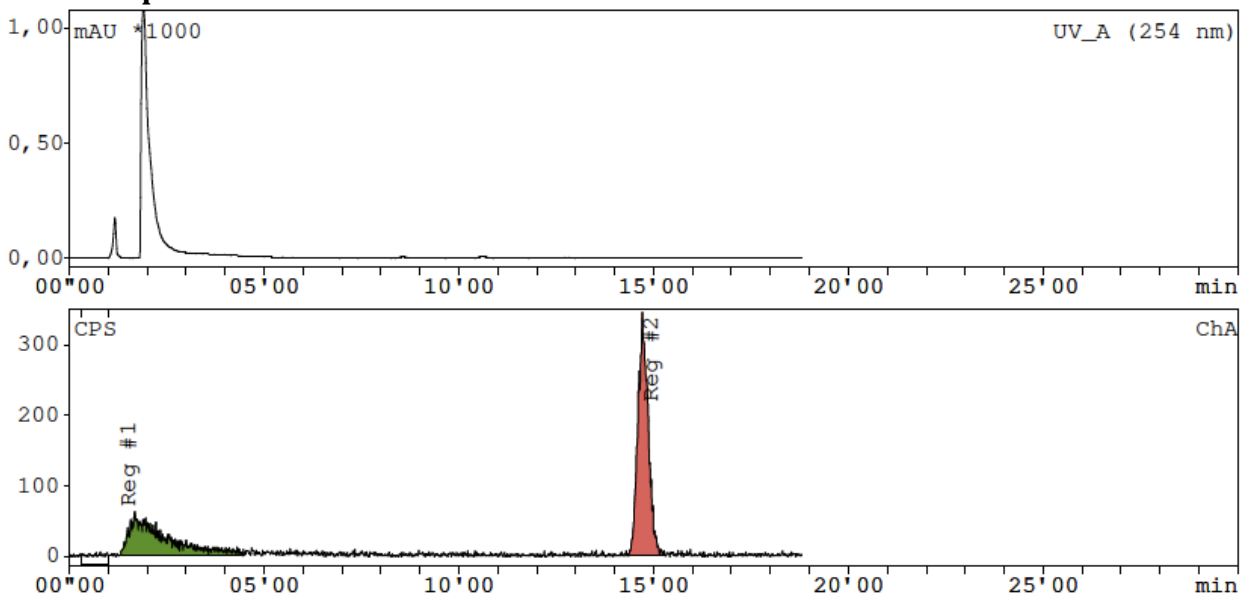
RCC

Entry	control	+PPh3	+N2	+PPh3, +N2
1	88,5	94,7	77,8	82,3
2	91,1	99,6	98,2	99,5

Entry	RCC Conditions	Average	Standard deviation	Repetitions
1	control	90	1	2
2	+PPh3	97	2	2
3	+N_2	88	10	2
4	+PPh3, +N2	91	9	2



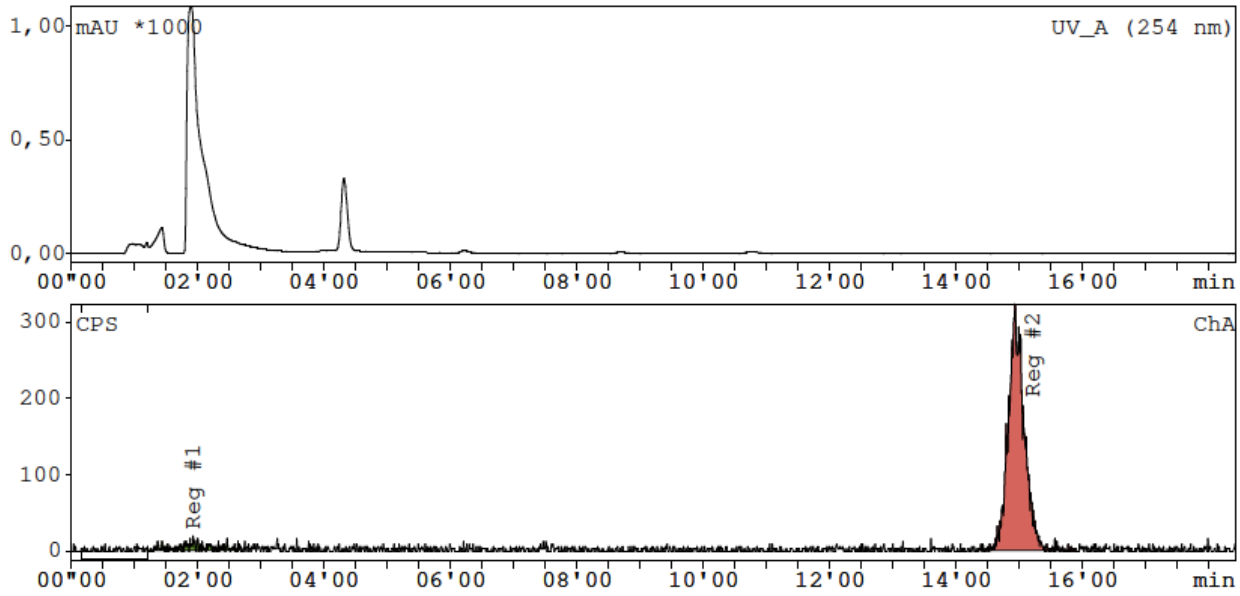
Standard procedure:



Integration ChA

Substance	R/T s	Type	Area Counts	%Area %
Reg #1	01'40	DD(M	3543,584	36,55
Reg #2	14'43	DD(M	6152,744	63,45
Sum in ROI			9696,328	100,00
Area (total)			10324,919	
BKG1			2,3210	

Standard procedure + 100 mol% PPh_3 + 1 min N_2



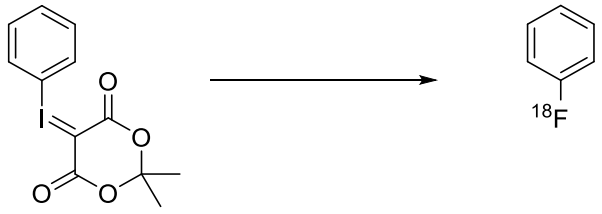
Integration ChA

Substance	R/T s	Type	Area Counts	%Area %
Reg #1	01'56	DD(M	295,604	5,24
Reg #2	14'56	DD(M	5342,043	94,76
Sum in ROI			5637,647	100,00
Area (total)			6231,453	
BKG1			1,7778	

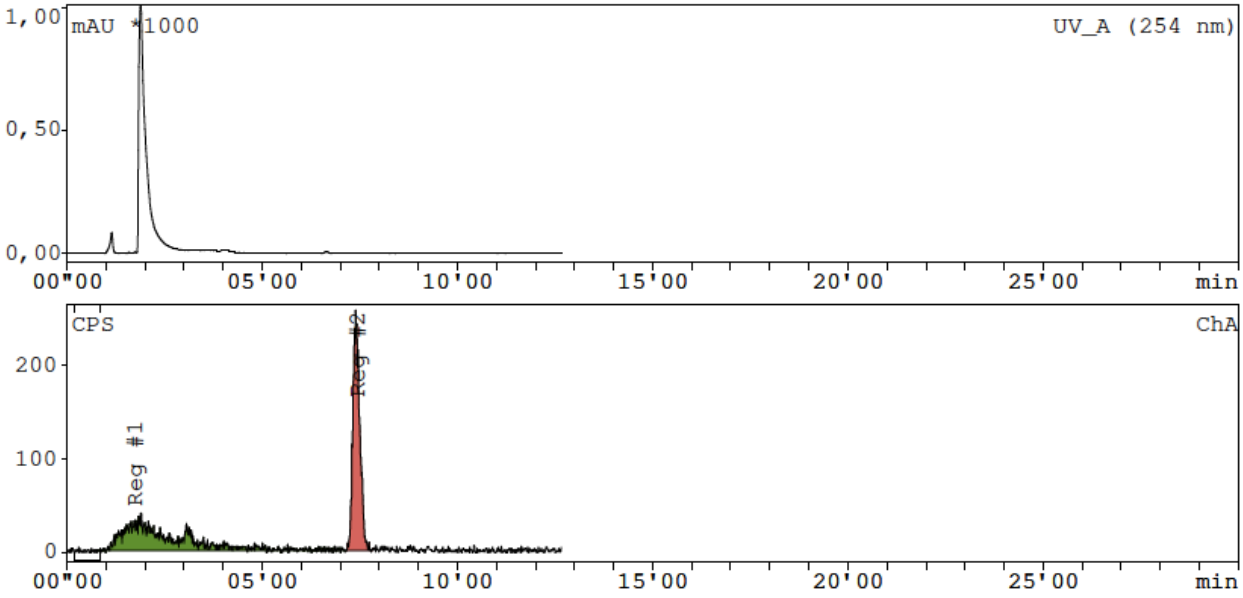
RCC

Entry	control	+PPh3	+N2	+PPh3, +N2
1	23,4	89	74,1	94,8
2	31,1	87,8	63,5	93,4
3			81,3	

Entry	RCC Conditions	Average	Standard deviation	Repetitions
1	control	27	4	2
2	+PPh3	88	1	2
3	+N_2	73	7	3
4	+PPh3, +N2	94	1	2



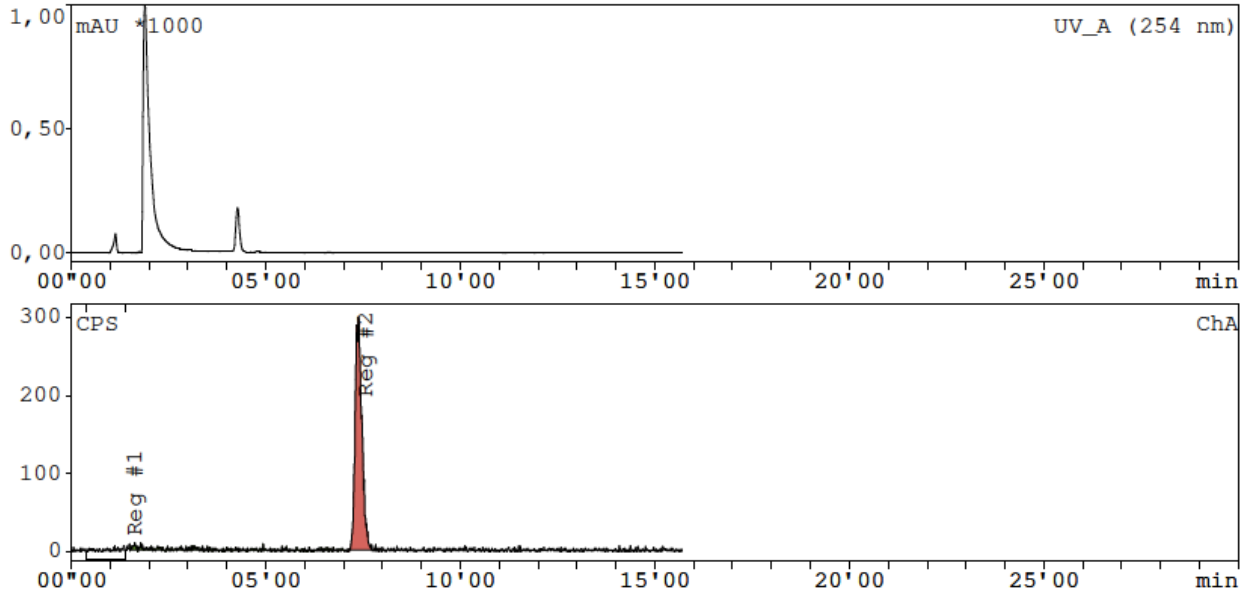
Standard procedure:



Integration ChA

Substance	R/T s	Type	Area Counts	%Area %
Reg #1	01'54	DD(M	2979,254	49,61
Reg #2	07'24	DD(M	3026,575	50,39
Sum in ROI			6005,829	100,00
Area (total)			6185,068	
BKG1			2,1235	

Standard procedure + 100 mol% PPh_3 + 1 min N_2



Integration ChA

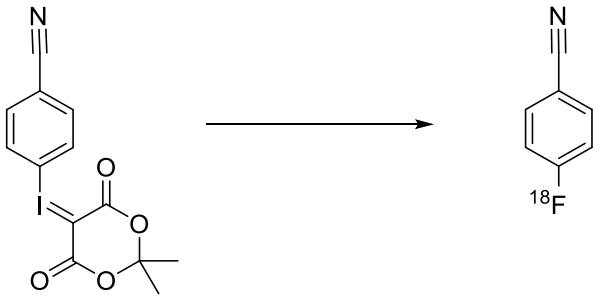
Substance	R/T s	Type	Area Counts	%Area %
Reg #1	01'47	DD(M	94,445	2,63
Reg #2	07'24	DD(M	3496,088	97,37
Sum in ROI			3590,533	100,00
Area (total)			3404,535	
BKG1			2,4660	

RCC

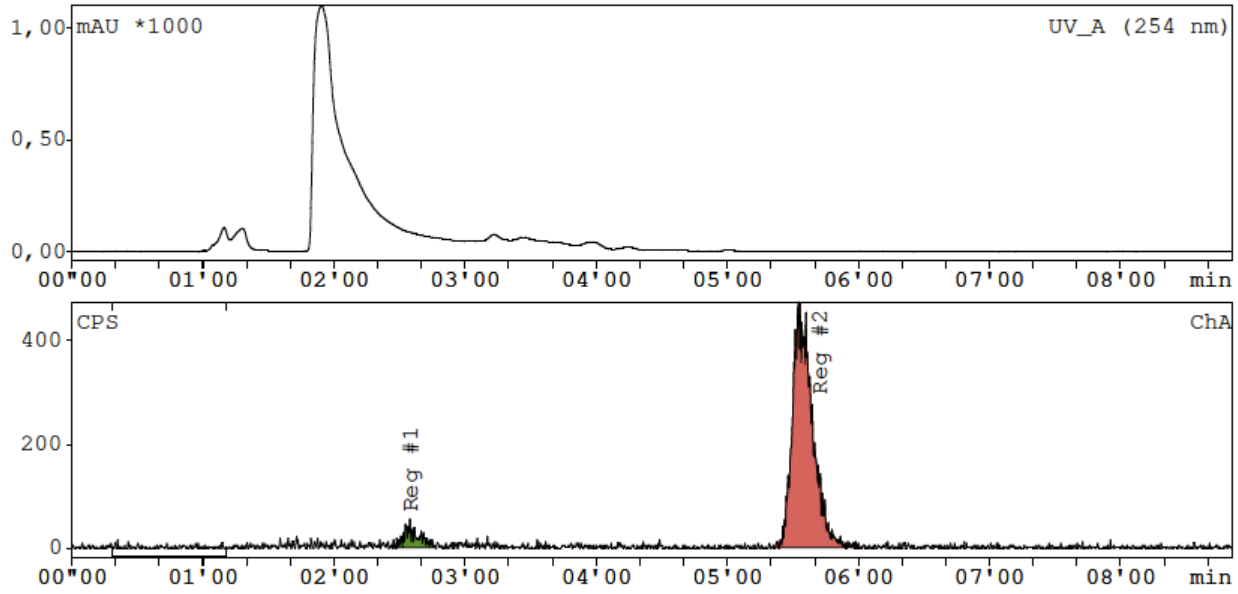
Entry	**control**	**+PPh3**	**+N2**	**+PPh3, +N2**
1	45,50	92,00	95,40	91,00
2	50,40	97,40	95,00	92,20
3	55,30	89,00		
4	47,80	93,40		

RCC

Entry	**Conditions**	**Average RCC**	**Standard deviation**	**Repetitions**
1	control	50	4	4
2	+PPh3	93	3	4
3	$+N_2$	95	0	2
4	+PPh3, +N2	92	1	2



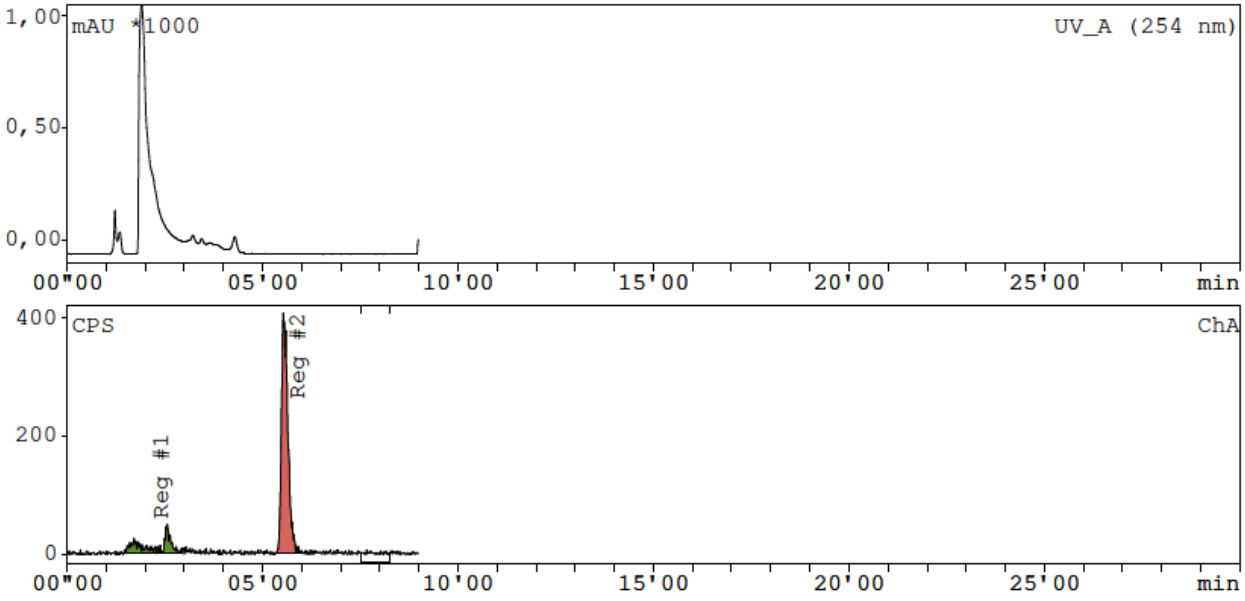
Standard procedure:



Integration ChA

Substance	R/T s	Type	Area Counts	%Area %
Reg #1	02'35	DD(M	319,345	6,22
Reg #2	05'33	DD(M	4811,178	93,78
Sum in ROI			5130,523	100,00
Area (total)			5512,745	
BKG1			2,6095	

Standard procedure + 100 mol% PPh_3 + 1 min N_2



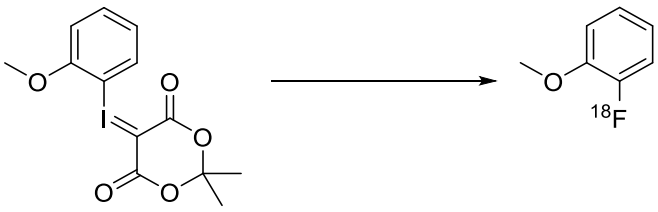
Integration ChA

Substance	R/T s	Type	Area Counts	%Area %
Reg #1	02'34	DD(M	930,623	16,88
Reg #2	05'33	DD(M	4581,938	83,12
Sum in ROI			5512,561	100,00
Area (total)			5672,381	
BKG1			2,6351	

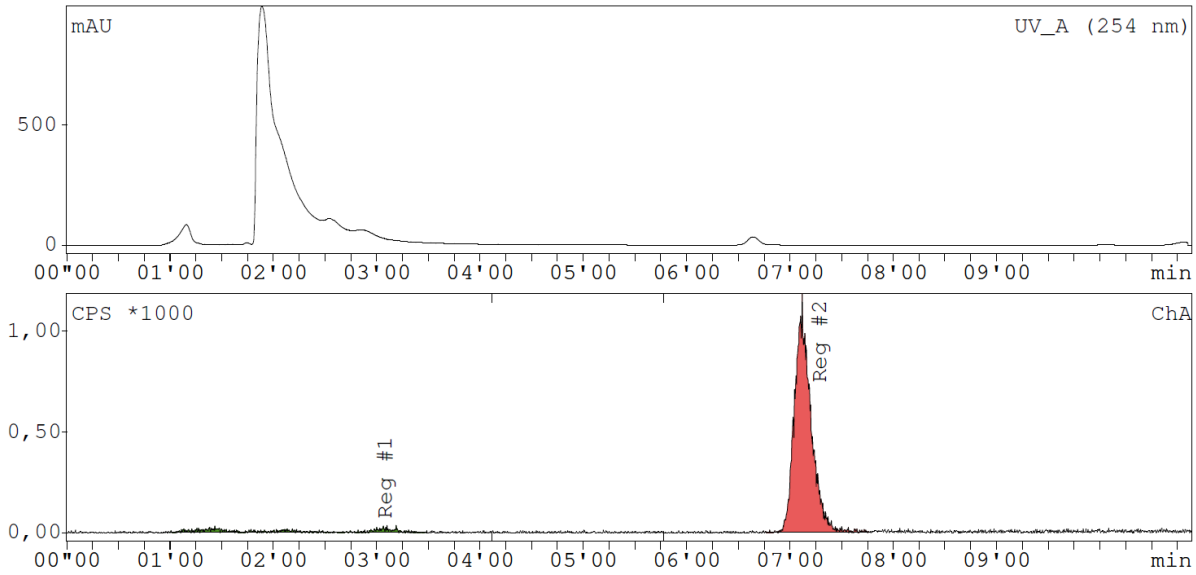
RCC

Entry	control	+PPh3	+N2	+PPh3, +N2
1	89,70	65,10	93,80	81,60
2	91,60	86,60	85,70	51,60
3	93,10	85,50		
4	92,50	78,20		

Entry	Conditions	Average RCC	Standard deviation	Repetitions
1	control	92	1	4
2	+PPh3	79	9	4
3	$+N_2$	90	4	2
4	+PPh3, +N	267	15	2



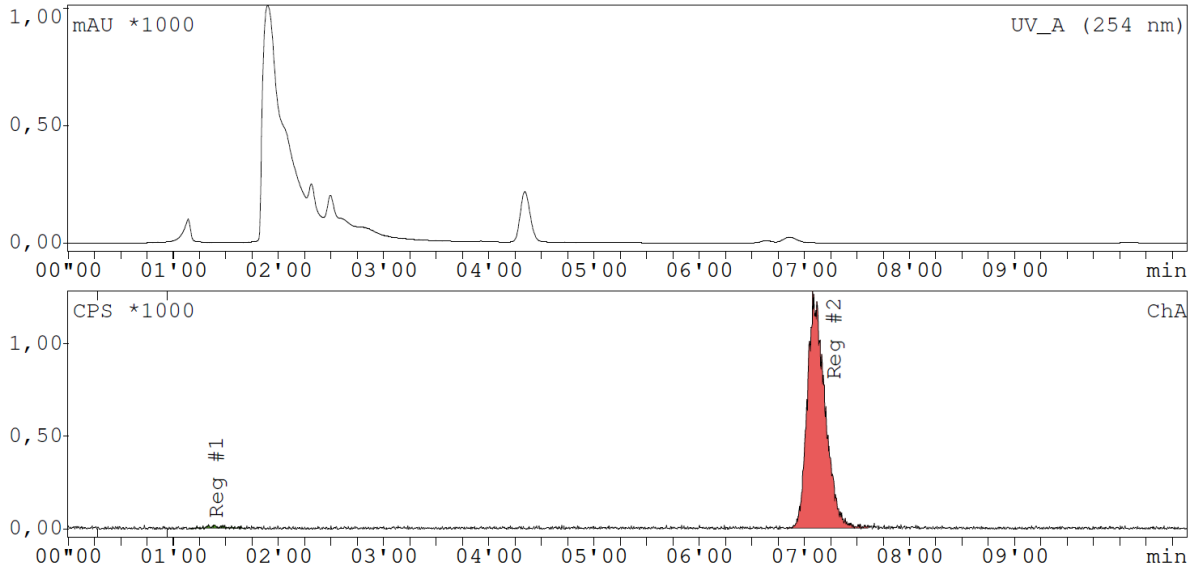
Standard procedure:



Integration ChA

Substance	R/T s	Type	Area Counts	%Area %
Reg #1	03'04	DD(M	718,18	5,48
Reg #2	07'07	DD(M	12389,02	94,52
Sum in ROI			13107,20	100,00
Area (total)			13869,06	
BKG1			2,226	
Remainder			761,85	5,49

Standard procedure + 100 mol% PPh_3 + 1 min N_2



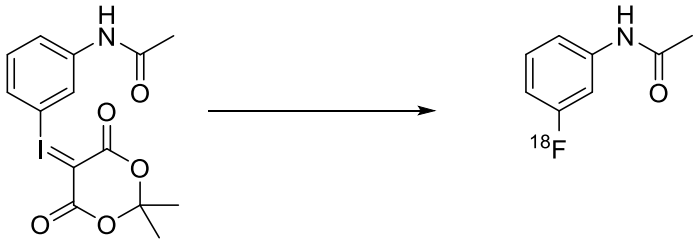
Integration ChA

Substance	R/T s	Type	Area Counts	%Area %
Reg #1	01'24	DD(M	123,42	0,83
Reg #2	07'05	DD(M	14758,08	99,17
Sum in ROI			14881,50	100,00
Area (total)			15385,11	
BKG1			4,336	
Remainder			503,60	3,27

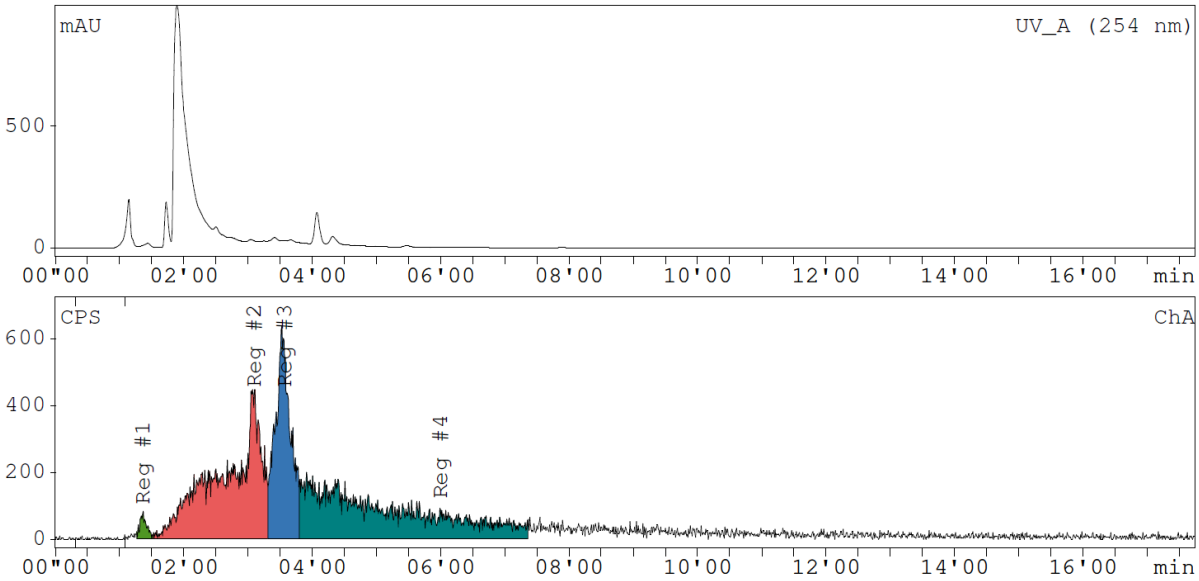
RCC

Entry	control	+PPh3	+N2	+PPh3, +N2
1	94.50	99.40	95.10	99.30
2	95.70	99.00	99.40	99.20

Entry	RCC Conditions	Average RCC	Standard deviation	Repetitions
1	control	95	1	2
2	+PPh3	99	0	2
3	+N_2	97	2	2
4	+PPh3, +N2	99	0	2



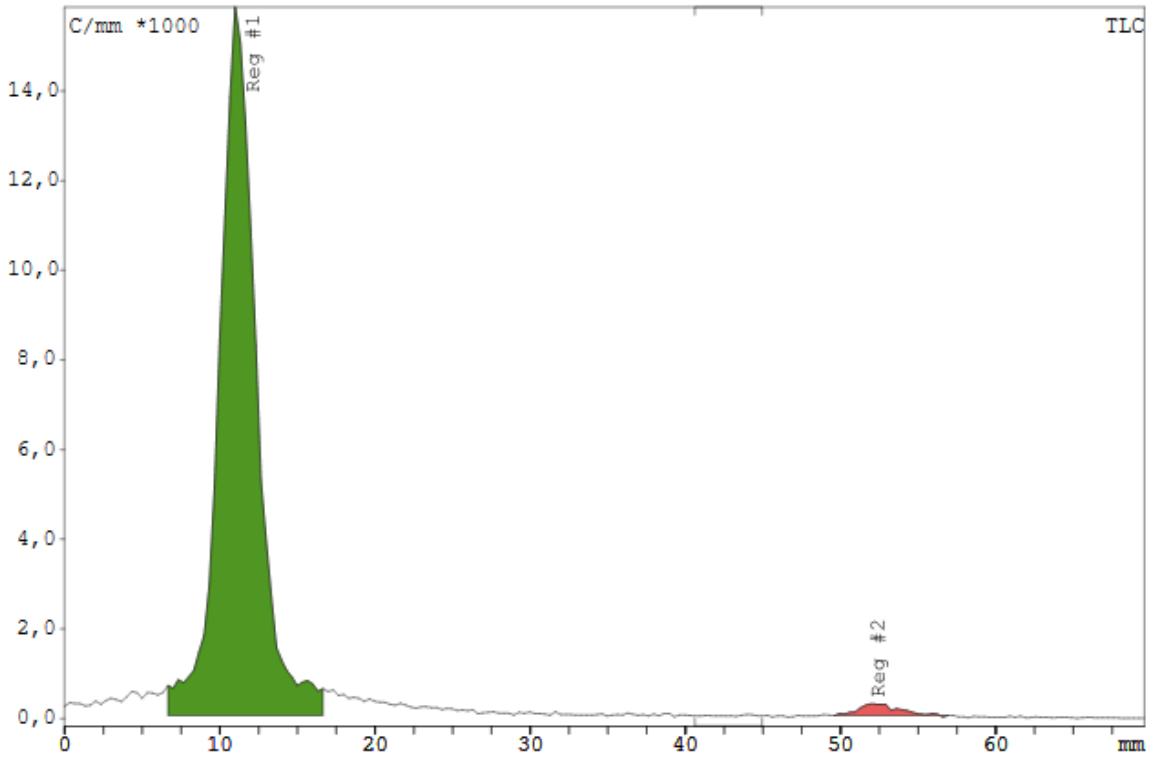
Standard procedure + 100 mol% PPh_3 + 1 min N_2



Integration ChA

Substance	R/T s	Type	Area Counts	%Area %
Reg #1	01'22	DD(M	588,10	1,29
Reg #2	03'04	DD(M	17204,68	37,72
Reg #3	03'32	DD(M	10417,21	22,84
Reg #4	07'11	DD(M	17398,23	38,15
Sum in ROI			45608,21	100,00
Area (total)			53987,94	
BKG1			1,970	
Remainder			8379,73	15,52

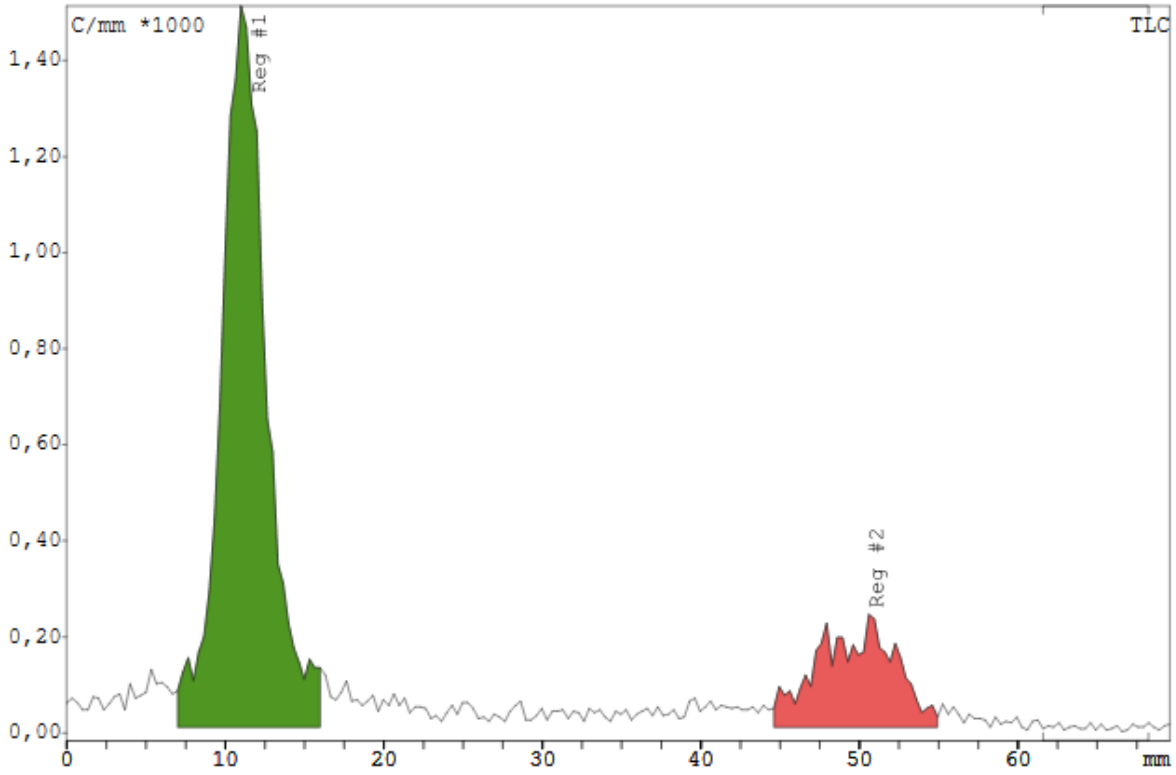
Standard procedure



Integration TLC

Substance	R/F	%Total	Type	Area	%Area
		%		Counts	%
Reg #1	0,157	87,98	DD	43995,54	98,22
Reg #2	0,748	1,59	DD	795,46	1,78
Sum in ROI				44791,00	
Total area				50007,38	
Area RF				49988,77	
BKG1				64,927	
Remainder RF				5197,77	10,40
Remainder (Tot)				5216,38	10,43

Standard procedure + 1 min N_2

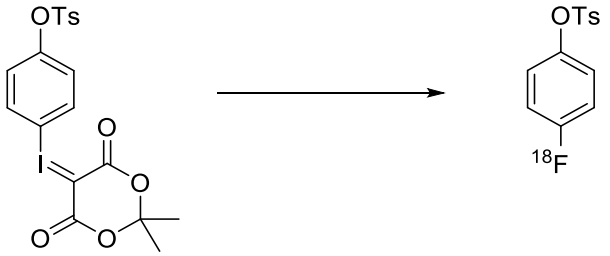


Integration TLC

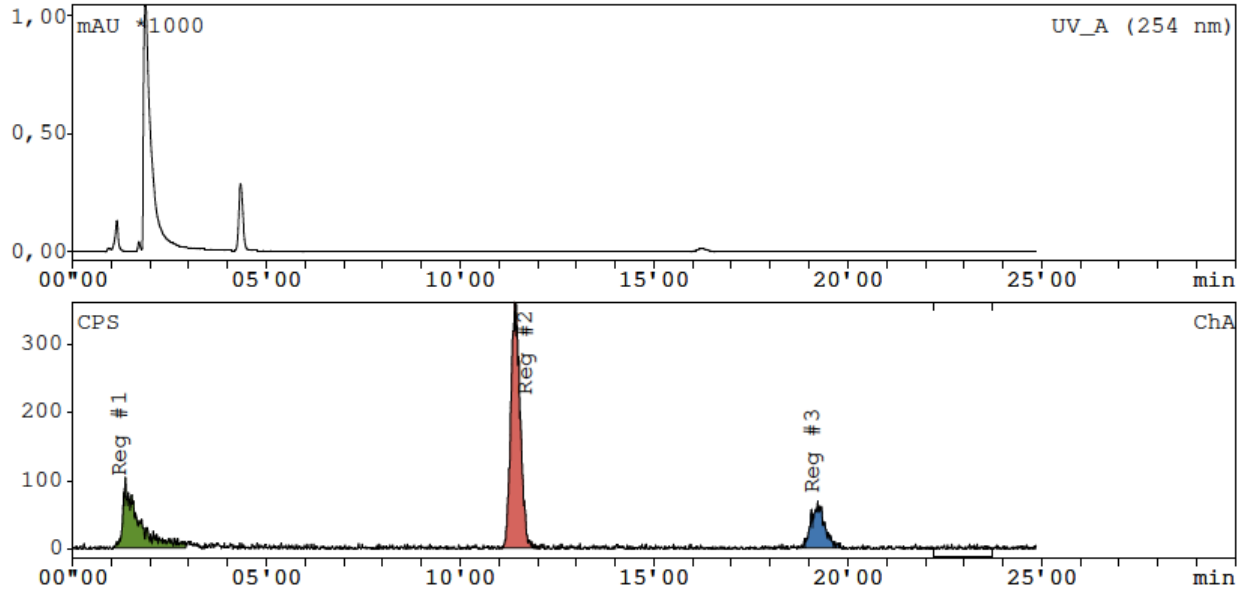
Substance	R/F	%Total	Type	Area	%Area
		%		Counts	%
Reg #1	0,157	62,56	DD	4958,700	79,44
Reg #2	0,729	16,19	DD	1283,100	20,56
Sum in ROI				6241,800	
Total area				7925,900	
Area RF				7927,000	
BKG1				11,7145	
Remainder RF				1685,20	21,26
Remainder (Tot)				1684,10	21,25

RCC

Entry	**control**	**+PPh3**	**+N2**	**+PPh3, +N2**
1	2	7	21	17



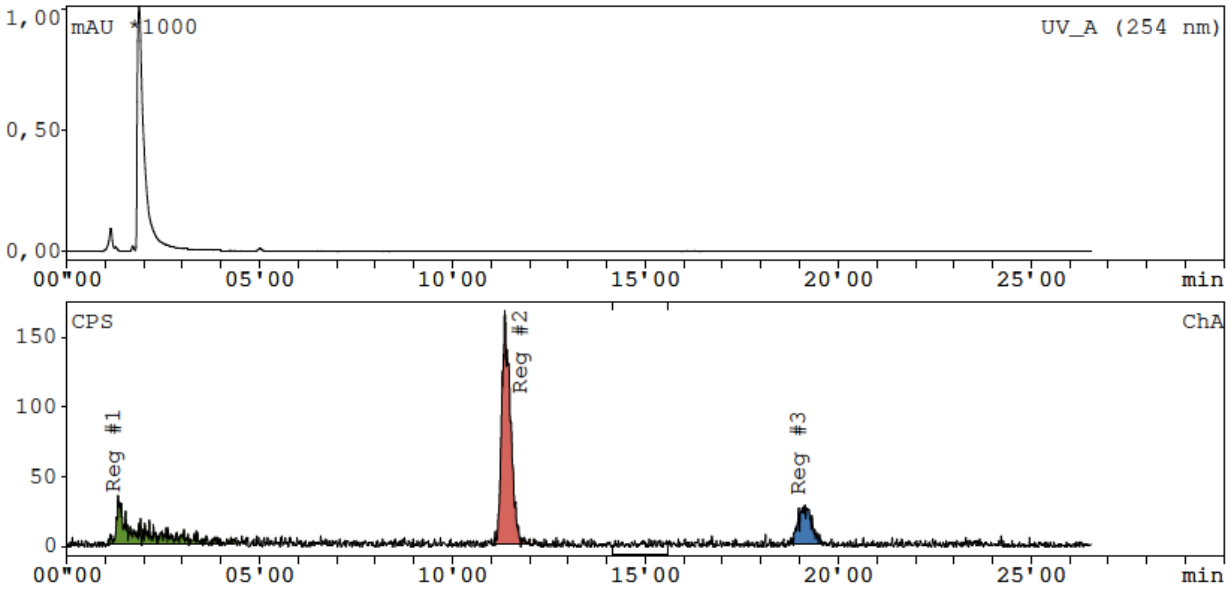
Standard procedure:



Integration ChA

Substance	R/T s	Type	Area Counts	%Area %
Reg #1	01'22	DD(M	2649,713	26,18
Reg #2	11'27	DD(M	5933,849	58,63
Reg #3	19'14	DD(M	1536,790	15,19
Sum in ROI			10120,352	100,00
Area (total)			10508,534	
BKG1			1,9829	

Standard procedure + 100 mol% PPh_3 + 1 min N_2



Integration ChA

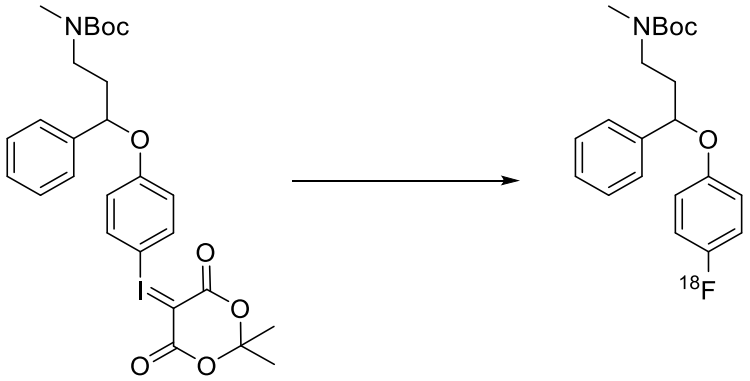
Substance	R/T s	Type	Area Counts	%Area %
Reg #1	01'21	DD(M	1111,807	25,62
Reg #2	11'22	DD(M	2583,639	59,54
Reg #3	19'08	DD(M	643,964	14,84
Sum in ROI			4339,410	100,00
Area (total)			4455,930	
BKG1			1,9861	

RCC

Entry	control	+PPh3	+N2	+PPh3, +N2
1	78,70	74,60	84,10	91,90
2	80,20	78,30	66,30	84,70
3	72,40	64,50		
4	70,70	54,60		
5	66,80	59,20		

Entry	RCC Conditions	Average RCC	Standard deviation	Product:Byproduct	Repetitions
1	control	74	5	2:7	5
2	+PPh3	66	9	2:7	5

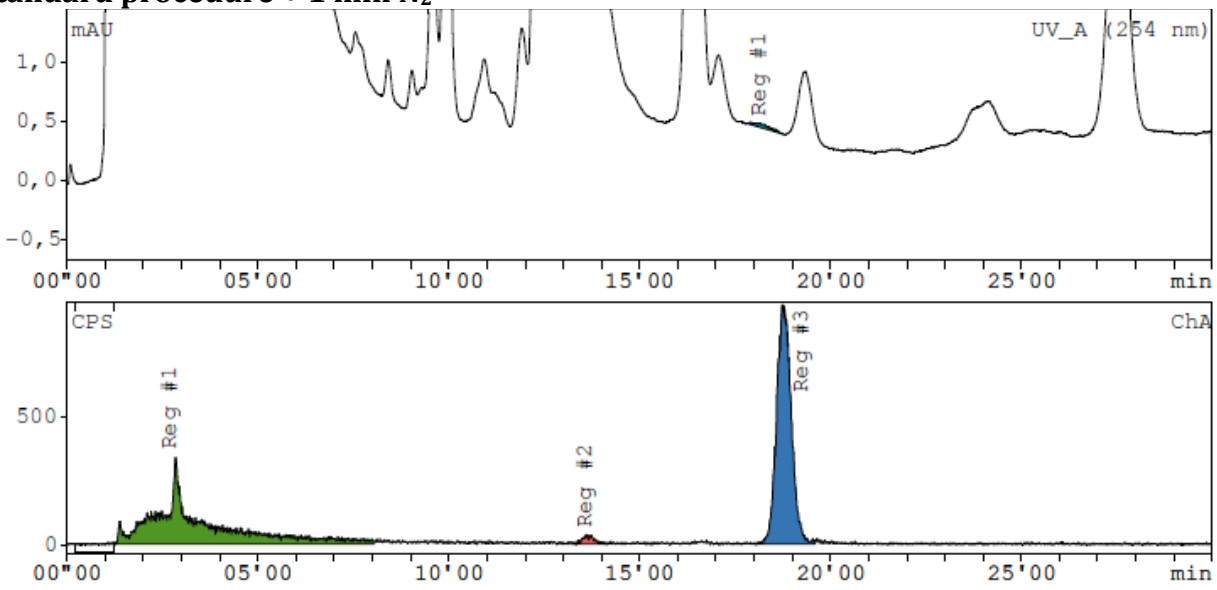
3	+N_2	75	9	1:5	2
4	+PPh3, +N2	88	4	1:5	2



Specific activity

271 MBq was produced with a specific activity of 274 GBq/µmol.

Standard procedure + 1 min N_2



Integration ChA

Substance	R/T s	Type	Area Counts	%Area %
Reg #1	02'51	DD(M	22193,96	46,57
Reg #2	13'43	DD(M	720,52	1,51
Reg #3	18'45	DD(M	24738,44	51,91
Sum in ROI			47652,92	100,00
Area (total)			50943,12	
BKG1			2,439	
Remainder			3290,21	6,46

RCC

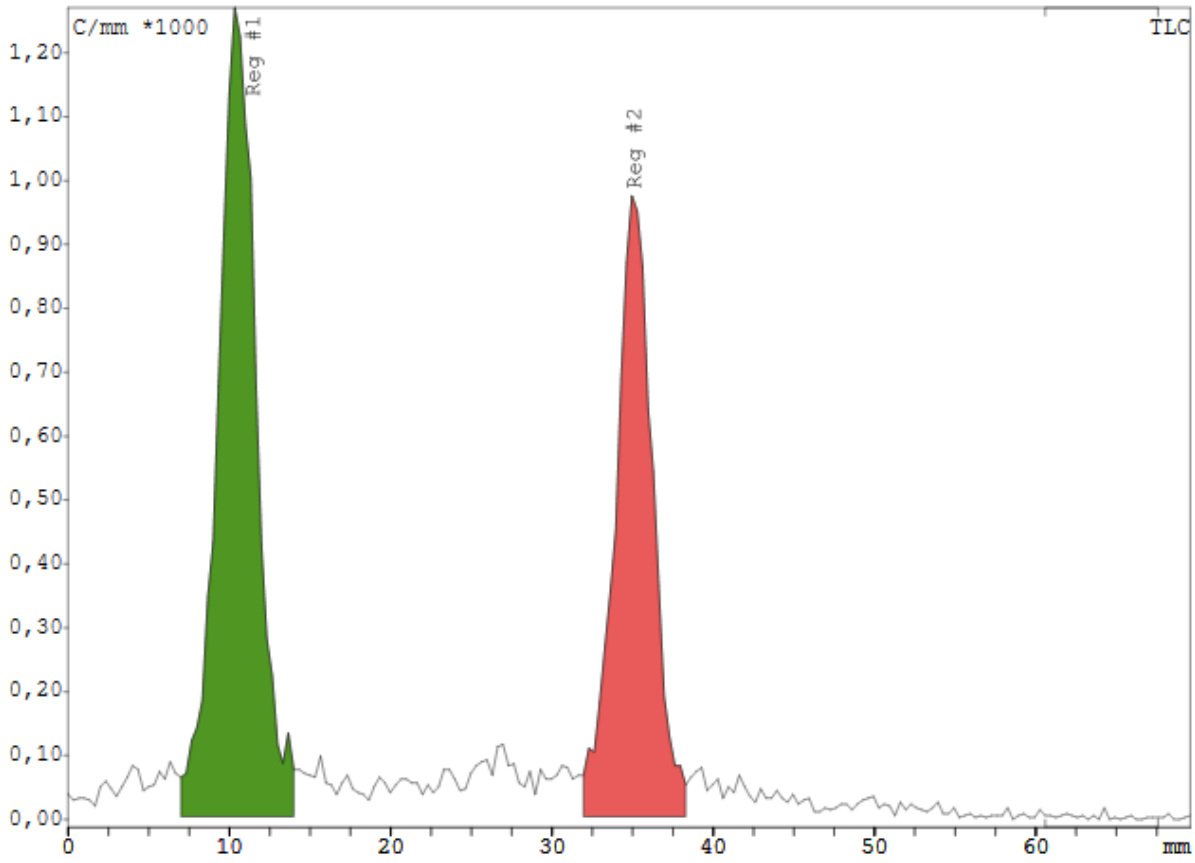
Entry	**control**	**+PPh3**	**+N2**	**+PPh3, +N2**
1	10,40	19,30	46,70	58,70
2	26,40	33,90	46,70	42,70
3	19,50	15,20	59,50	56,00

Entry	**RCC Conditions**	**Average RCC**	**Standard deviation**	**Repetitions**
1	control	19	7	3
2	+PPh3	23	8	3
3	+N_2	51	6	3
4	+PPh3, +N2	52	7	3

Entry	**Decay corr. Yield**	**n.d.c. Yield**	**MBq of product**	**RCP**
1	0,30	0,21	131	<95%
2	0,62	0,43	271	<95%
3	0,36	0,25	106	<95%

Entry	**Average n.d.c. yield %**	**Standard deviation**
1	0,29	0,10

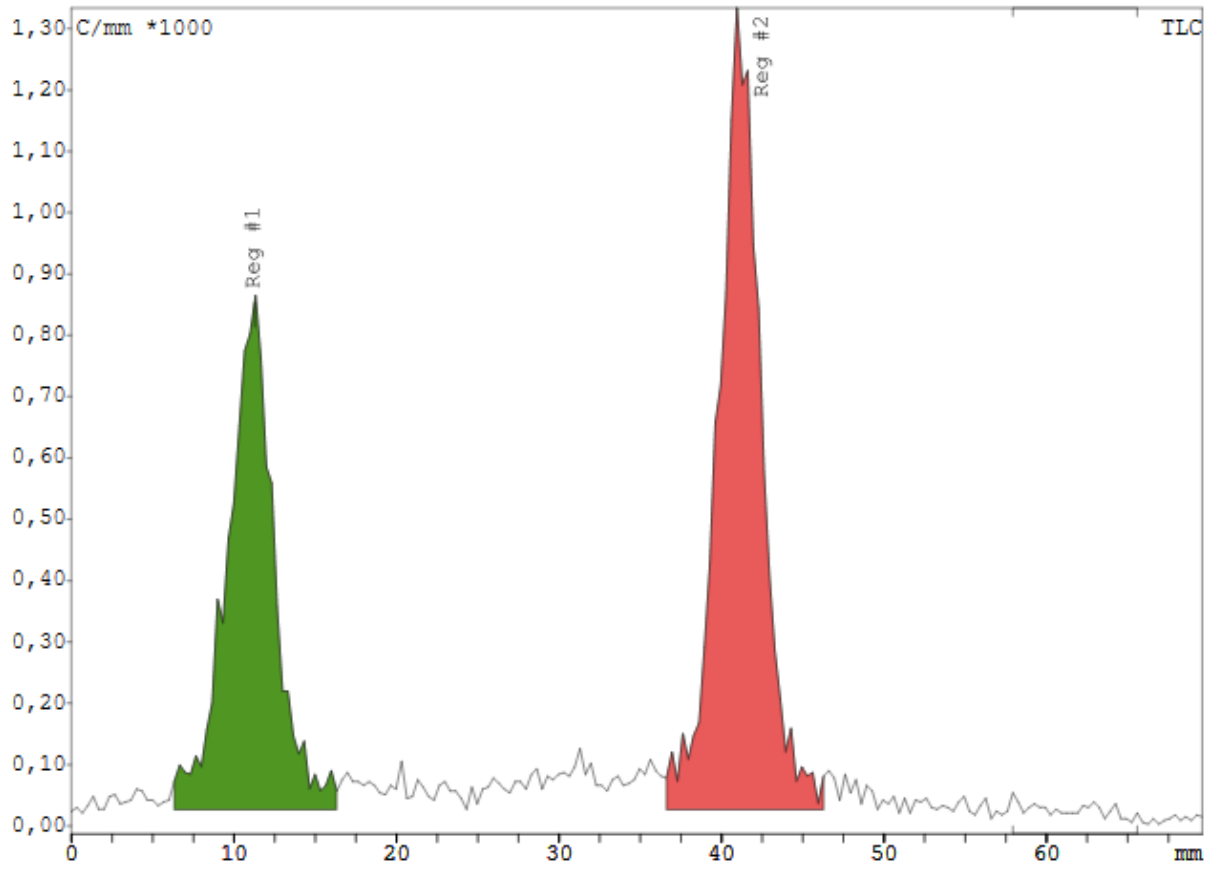
Standard procedure:



Integration TLC

Substance	R/F	%Total	Type	Area	%Area
		%		Counts	%
Reg #1	0,152	43,67	DD	3514,000	57,29
Reg #2	0,500	32,56	DD	2619,762	42,71
Sum in ROI				6133,762	
Total area				8046,381	
Area RF				8046,000	
BKG1				4,1480	
Remainder RF				1912,24	23,77
Remainder (Tot)				1912,62	23,77

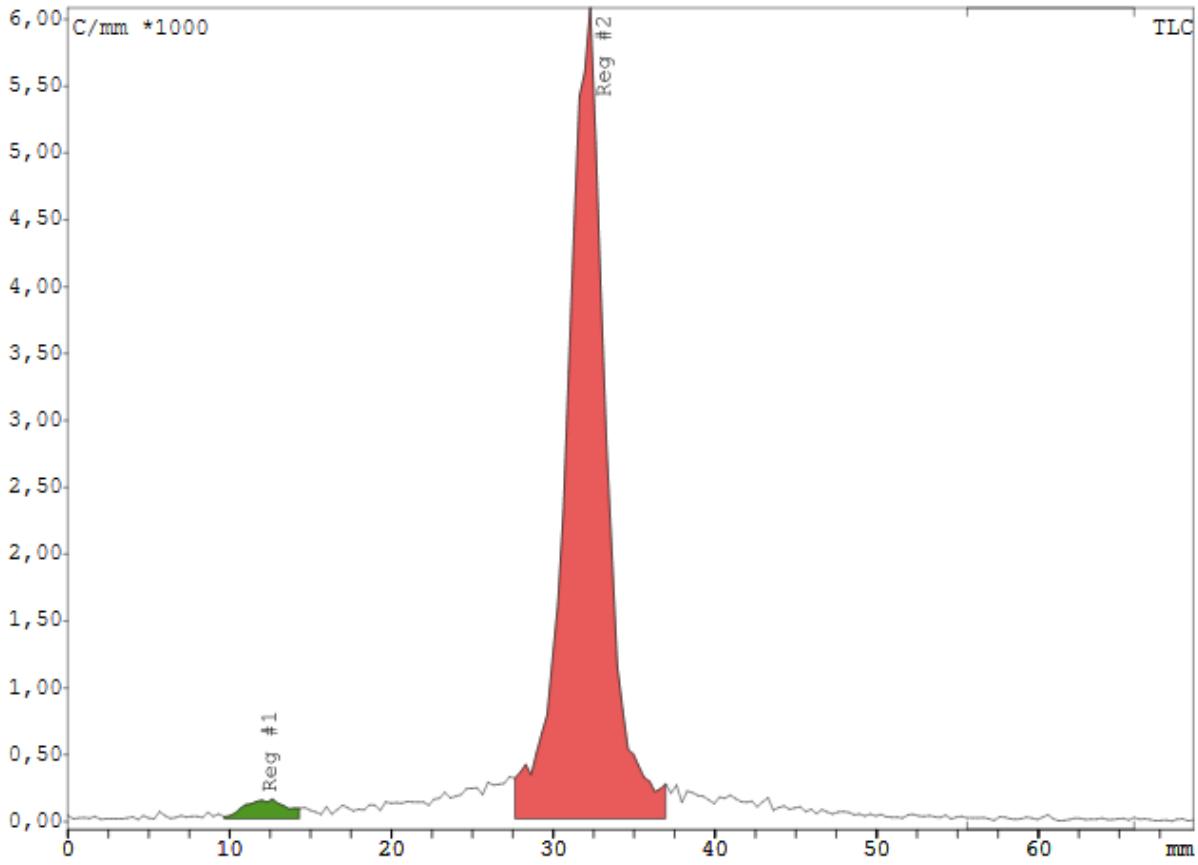
Standard procedure + 100 mol% PPh_3 + 1 min N_2



Integration TLC

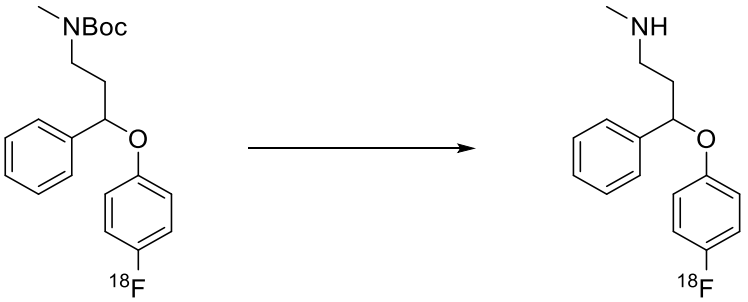
Substance	R/F	%Total	Type	Area	%Area
		%		Counts	%
Reg #1	0,157	35,52	DD	2787,826	41,32
Reg #2	0,590	50,45	DD	3959,565	58,68
Sum in ROI				6747,391	
Total area				7848,522	
Area RF				7845,783	
BKG1				26,2499	
Remainder RF				1098,39	14,00
Remainder (Tot)				1101,13	14,03

Standard procedure + 100 mol% PPh_3 + 1 min N_2, C18 purified.

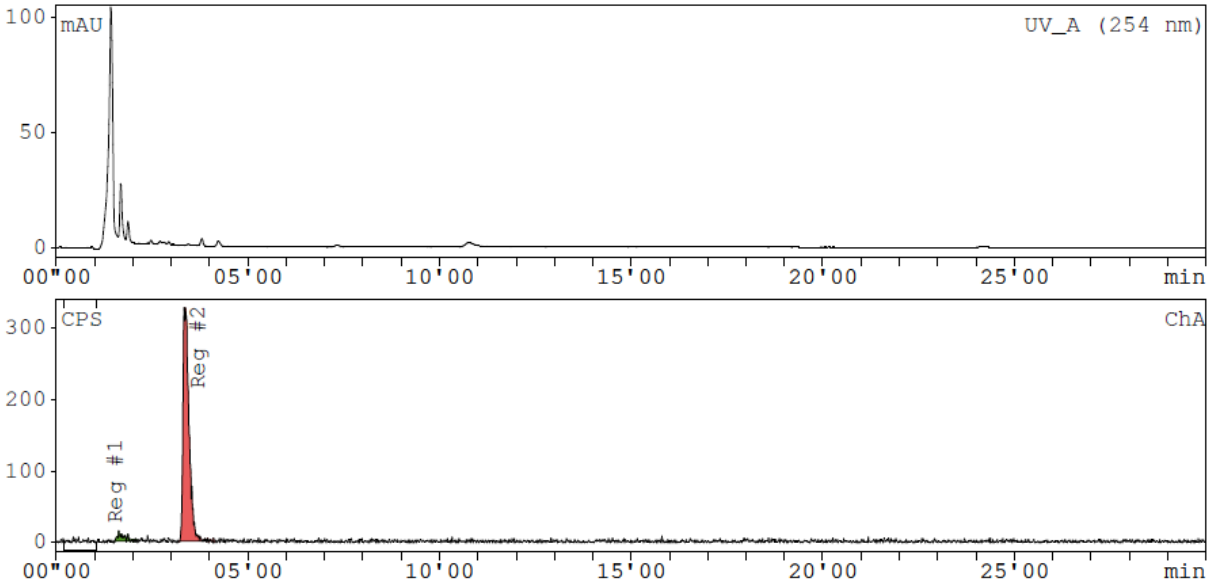


Integration TLC

Substance	R/F	%Total	Type	Area	%Area
		%		Counts	%
Reg #1	0,176	2,00	DD	418,23	2,39
Reg #2	0,457	81,72	DD	17061,45	97,61
Sum in ROI				17479,68	
Total area				20876,87	
Area RF				20871,39	
BKG1				22,479	
Remainder RF				3391,71	16,25
Remainder (Tot)				3397,19	16,27

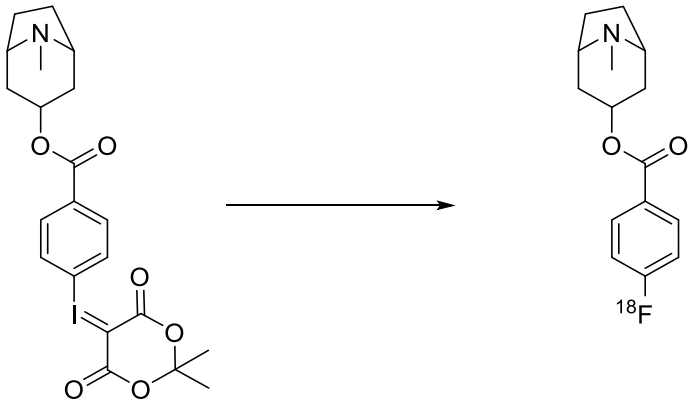


10 minutes at 100 °C in 6M HCl (THF:H_2O, 1:1)

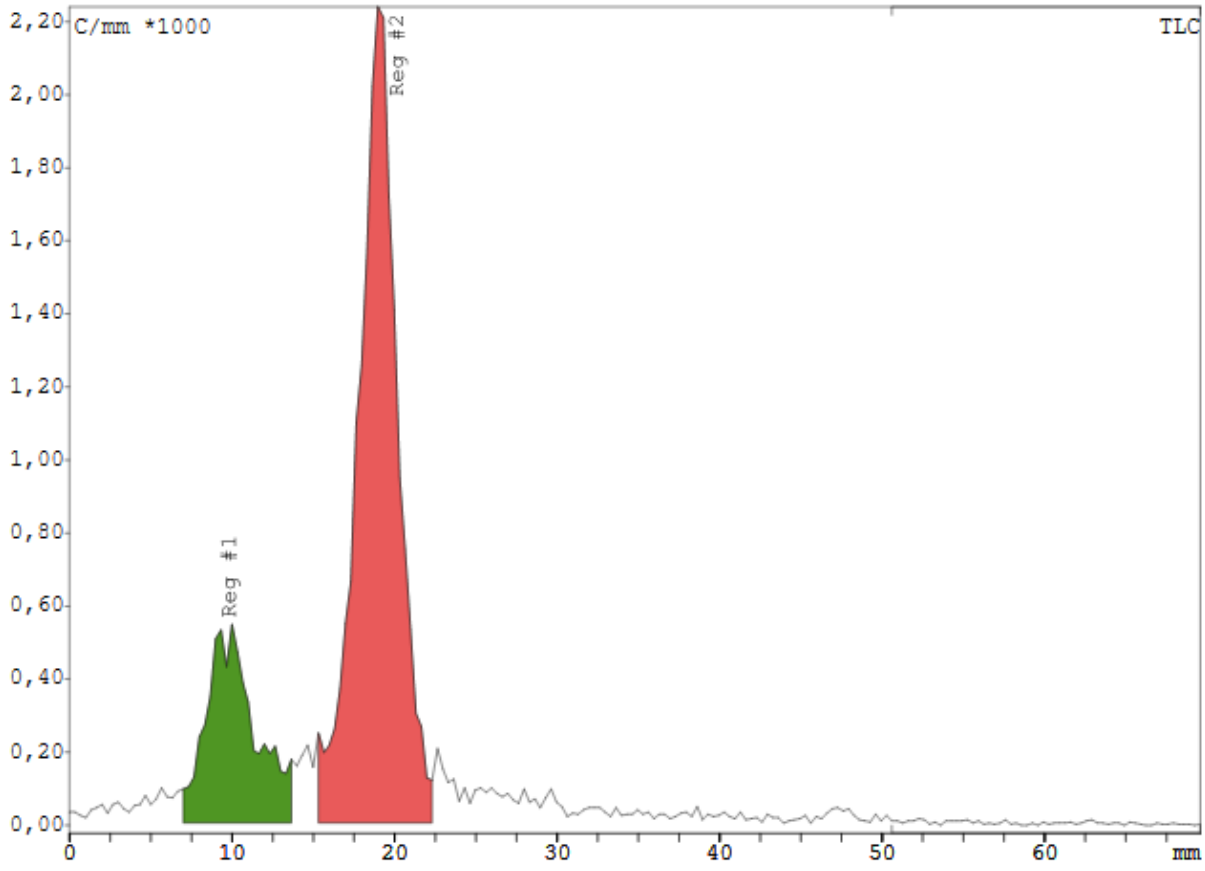


Integration ChA

Substance	R/T s	Type	Area Counts	%Area %
Reg #1	01'42	DD(M	140,465	3,88
Reg #2	03'23	DD(M	3475,812	96,12
Sum in ROI			3616,277	100,00
Area (total)			3359,639	
BKG1			2,0809	
Remainder			-256,64	-7,64



Standard procedure: (TLC plate was developed to 45 mm)



Integration TLC

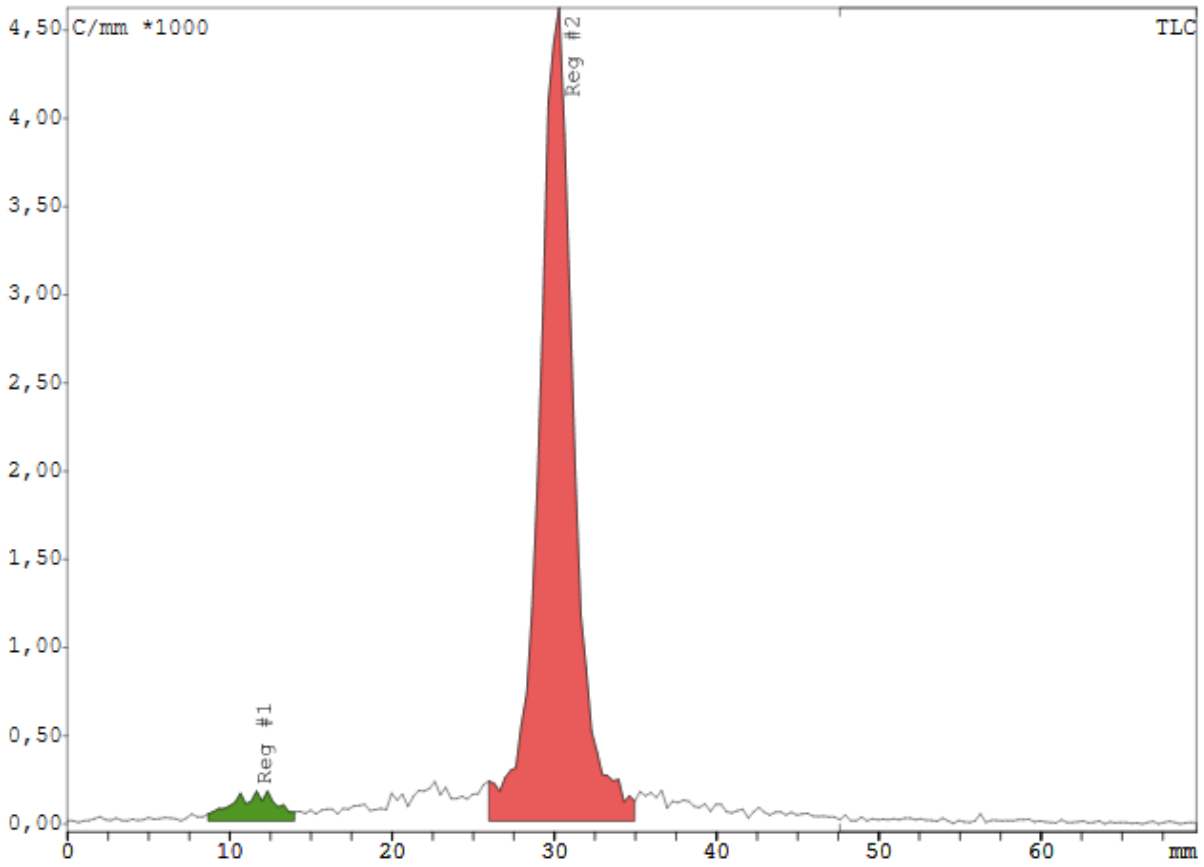
Substance	R/F	%Total	Type	Area	%Area
		%		Counts	%
Reg #1	0,138	18,85	DD	1872,897	22,95
Reg #2	0,271	63,29	DD	6287,741	77,05
Sum in ROI				8160,638	
Total area				9934,569	
Area RF				9932,414	
BKG1				6,4735	
Remainder RF				1771,78	17,84
Remainder (Tot)				1773,93	17,86

RCC

Entry	**control**	**+PPh3**	**+N2**	**+PPh3, +N2**
1	87,00	88,40	96,70	95,70
2	77,10	87,50	95,20	91,30

Entry	**RCC Conditions**	**Average RCC**	**Standard deviation**	**Repetitions**
1	control	82	5	2
2	+PPh3	88	0	2
3	+N_2	96	1	2
4	+PPh3, +N2	94	2	2

Standard procedure + 100 mol% PPh_3 + 1 min N_2

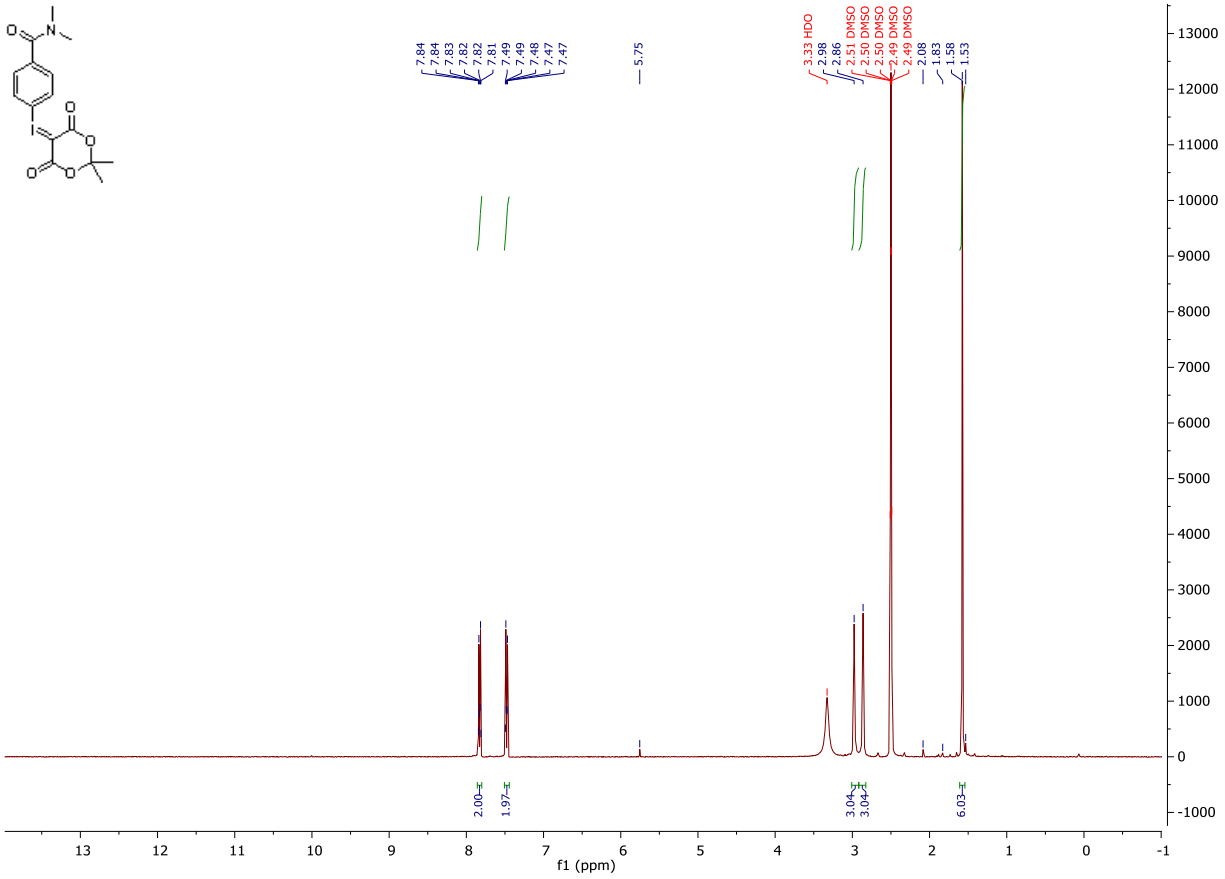


Integration TLC

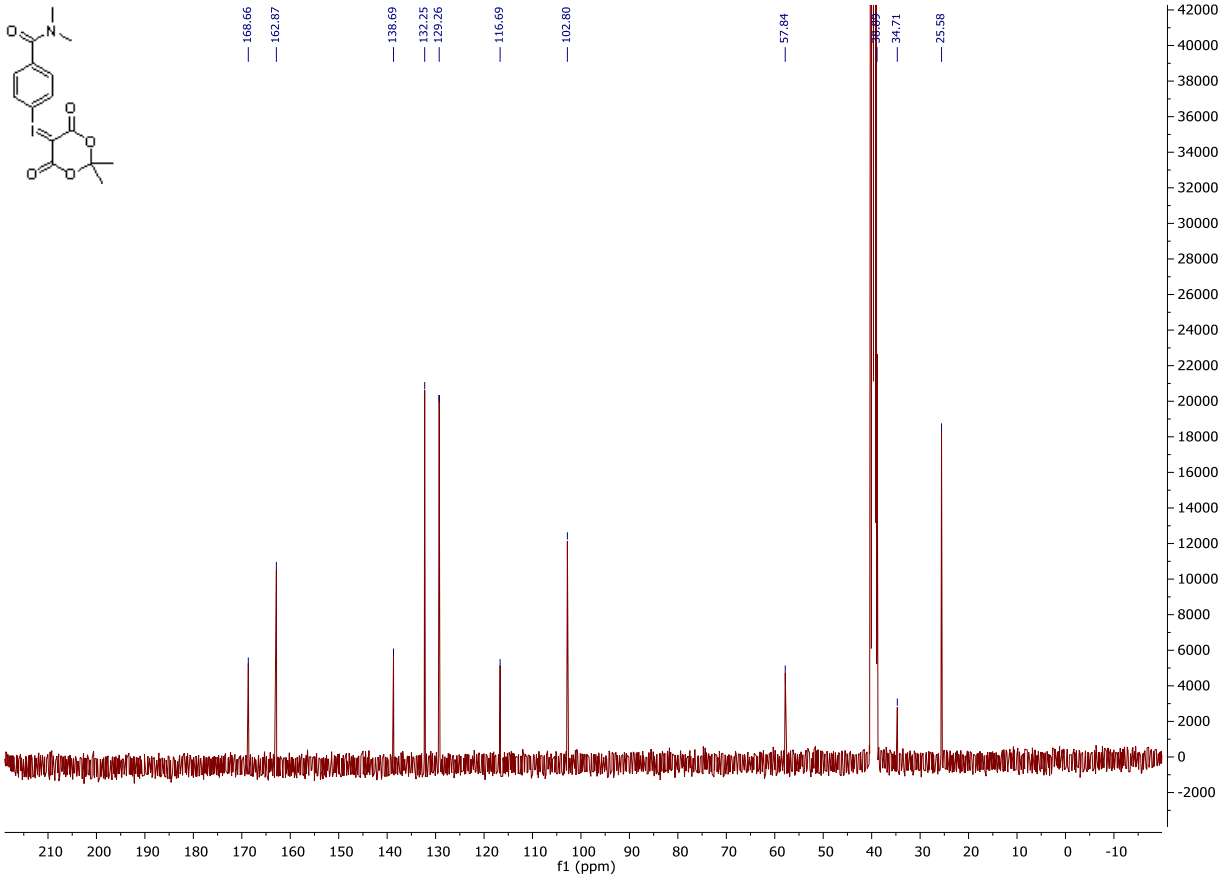
Substance	R/F	%Total	Type	Area	%Area
		%		Counts	%
Reg #1	0,171	3,63	DD	521,78	4,32
Reg #2	0,433	80,25	DD	11548,06	95,68
Sum in ROI				12069,84	
Total area				14389,39	
Area RF				14386,69	
BKG1				17,126	
Remainder RF				2316,85	16,10
Remainder (Tot)				2319,55	16,12

10. 1H, 13C and 19F NMR

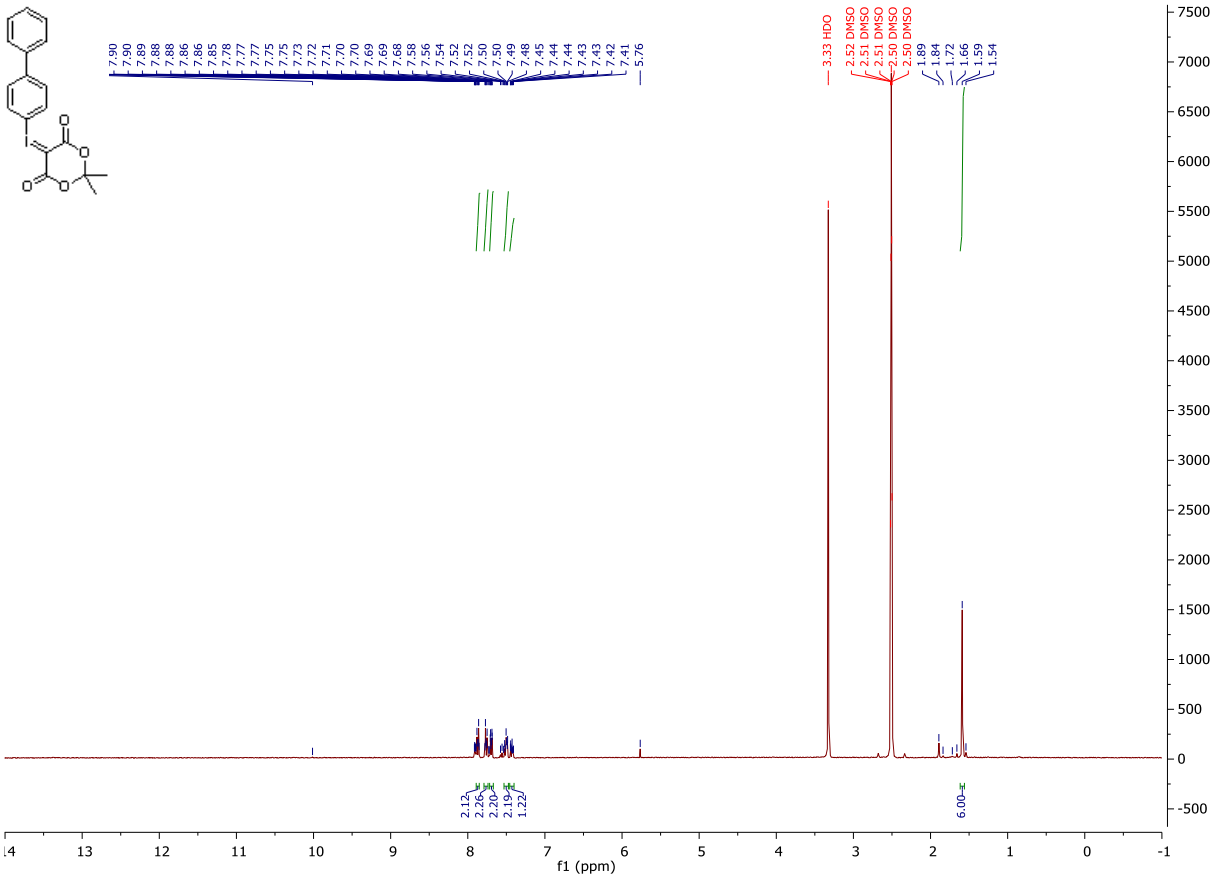
4-((2,2-dimethyl-4,6-dioxo-1,3-dioxan-5-ylidene)-l3-iodaneyl)-N,N-dimethylbenzamide



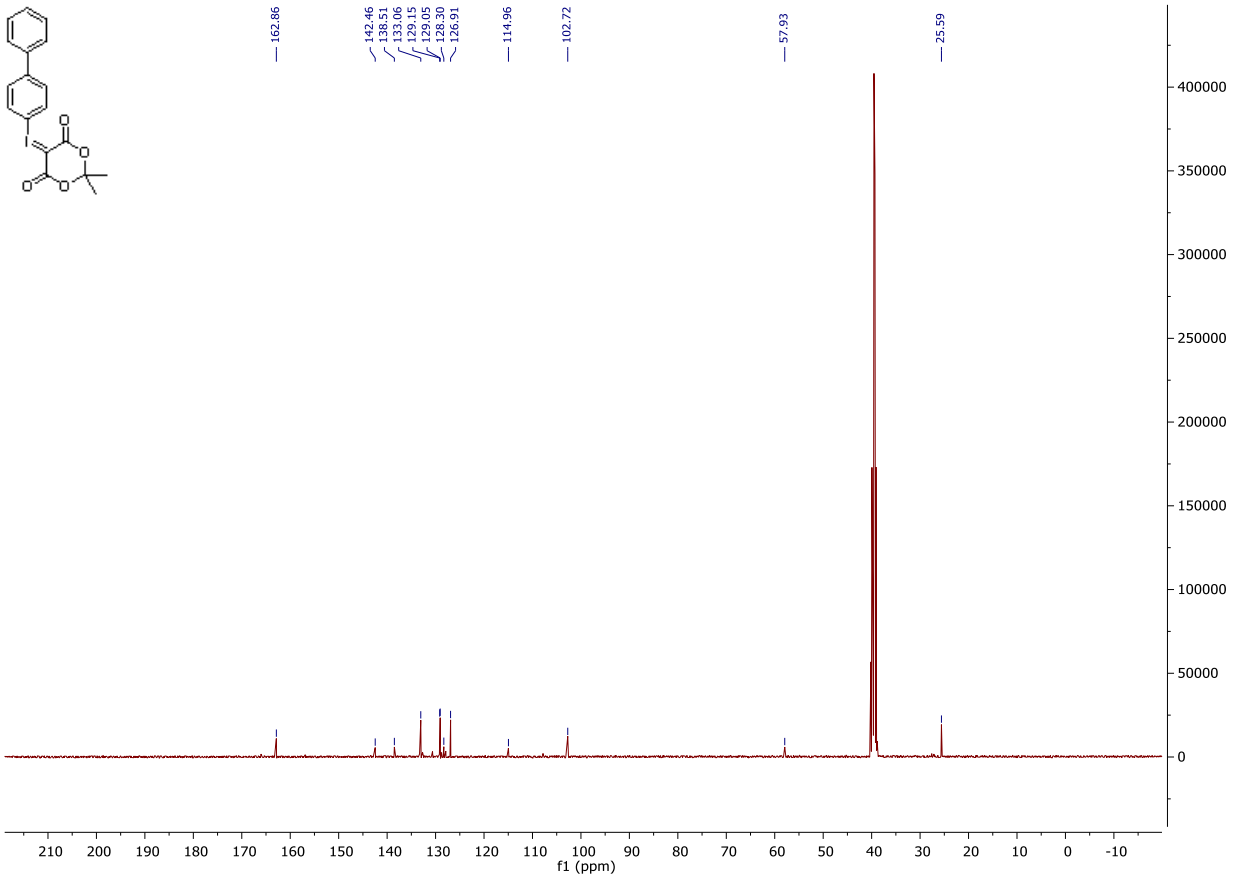
4-((2,2-dimethyl-4,6-dioxo-1,3-dioxan-5-ylidene)-l3-iodaneyl)-N,N-dimethylbenzamide



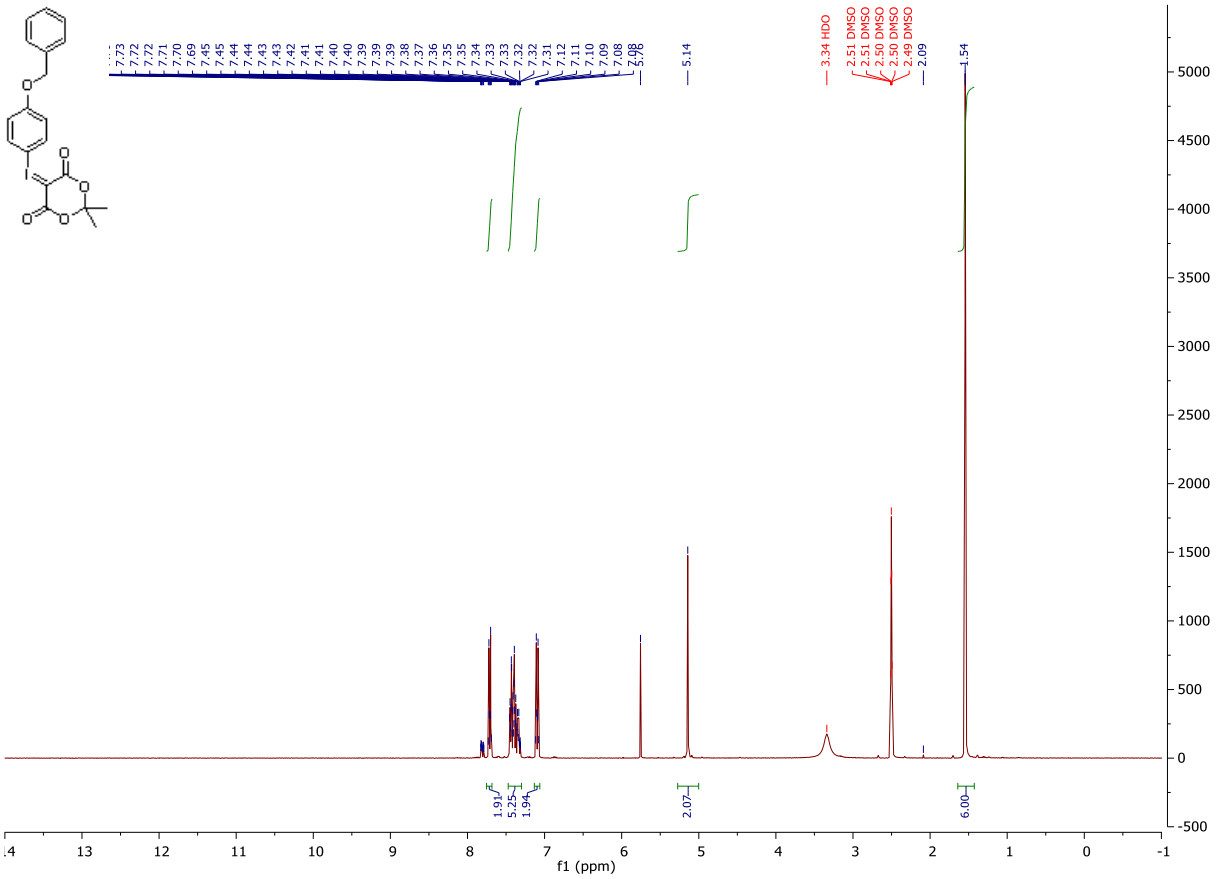
5-([1,1'-biphenyl]-4-yl-l3-iodaneylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione



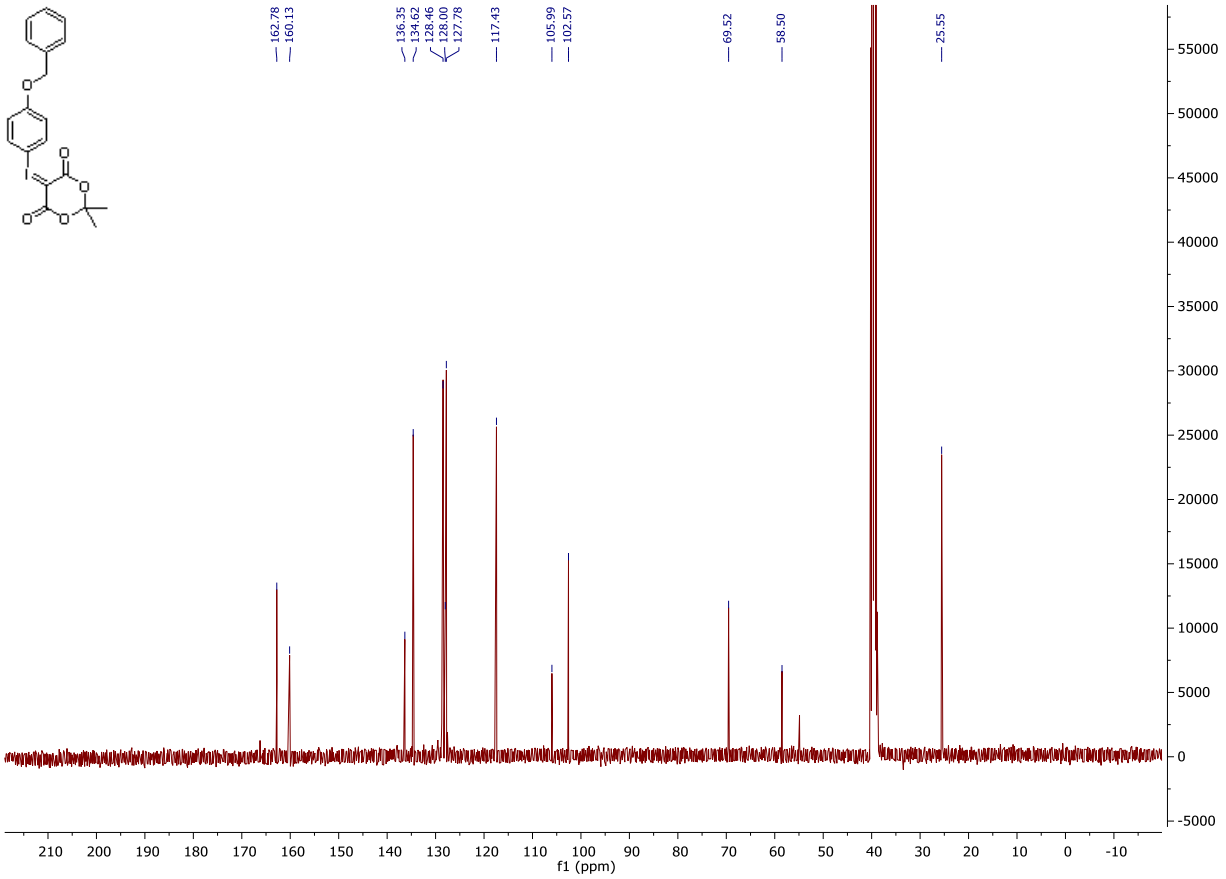
5-([1,1'-biphenyl]-4-yl-l3-iodaneylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione



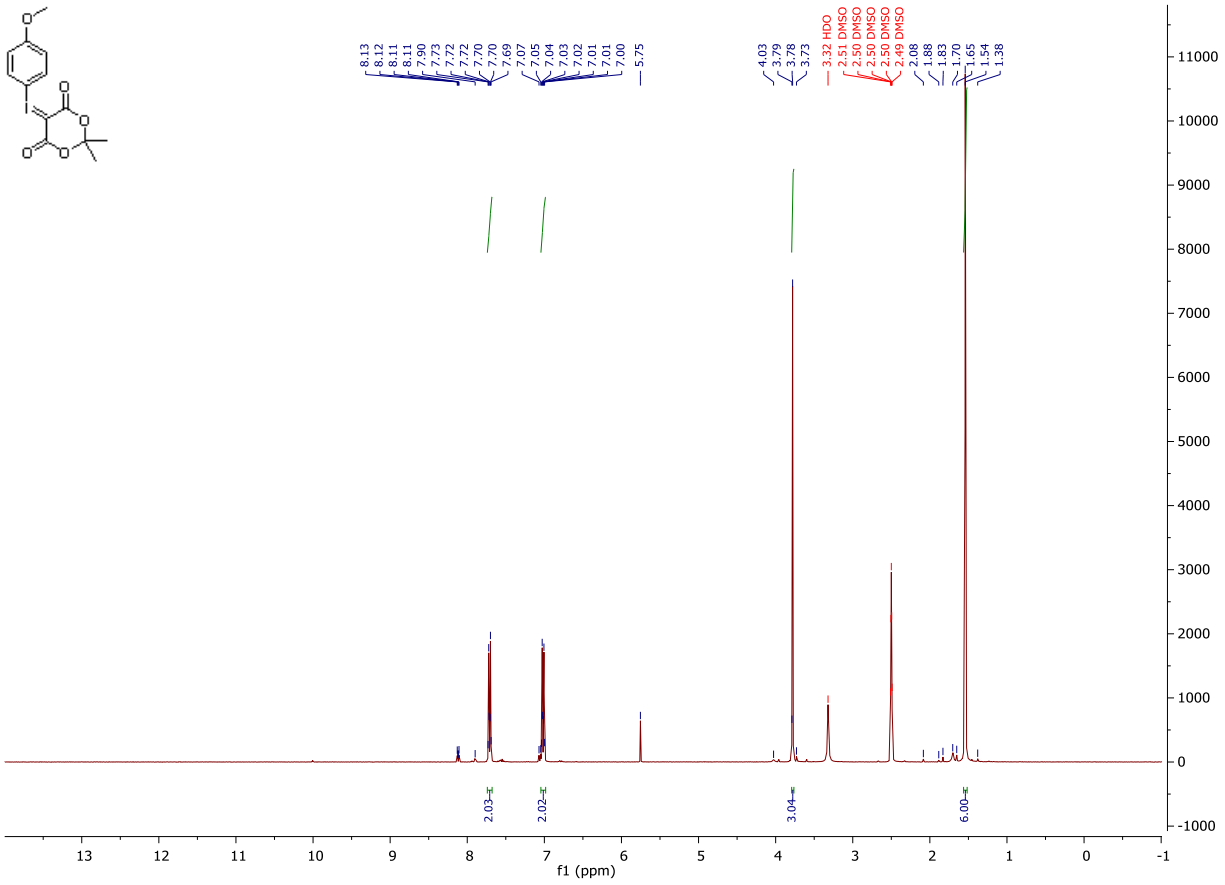
5-((4-(benzyloxy)phenyl)-l3-iodaneylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione



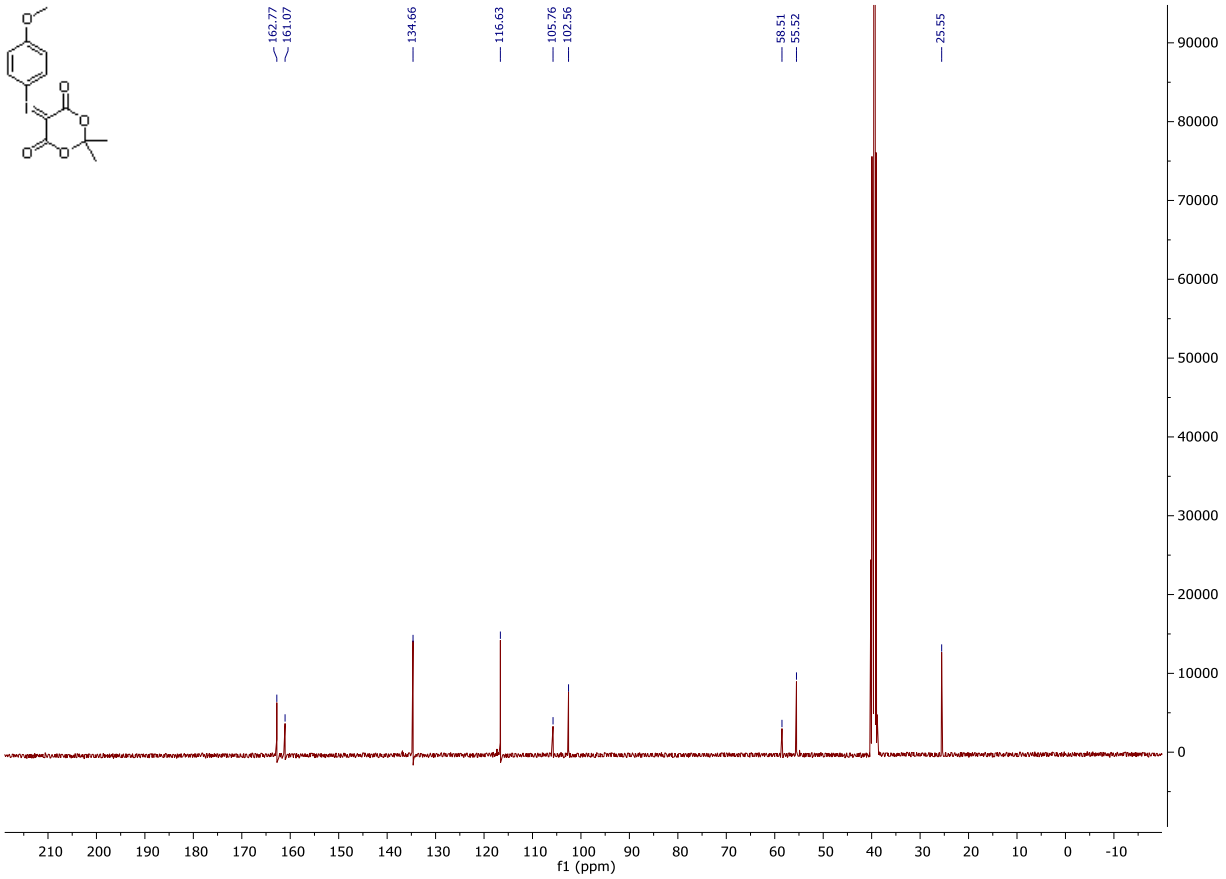
5-((4-(benzyloxy)phenyl)-l3-iodaneylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione



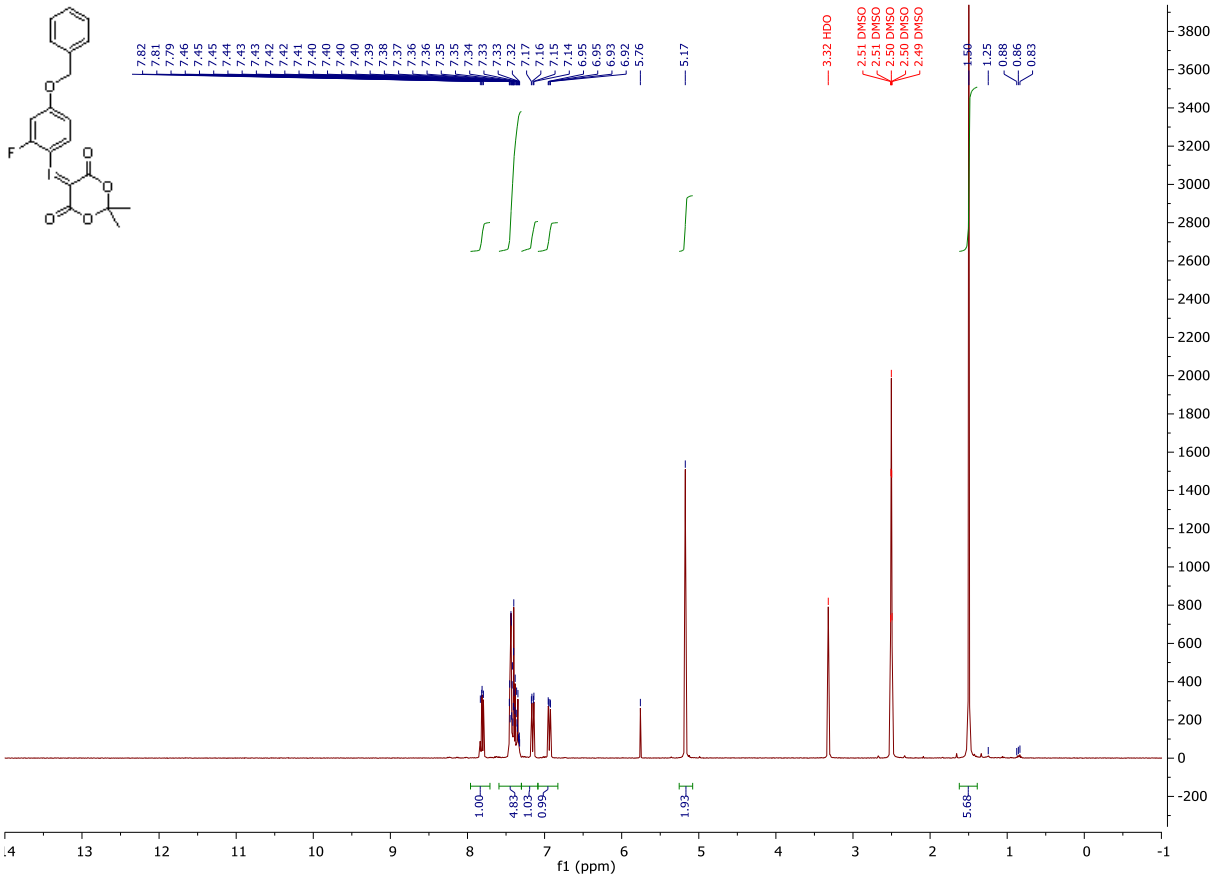
5-((4-methoxyphenyl)-l3-iodaneylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione



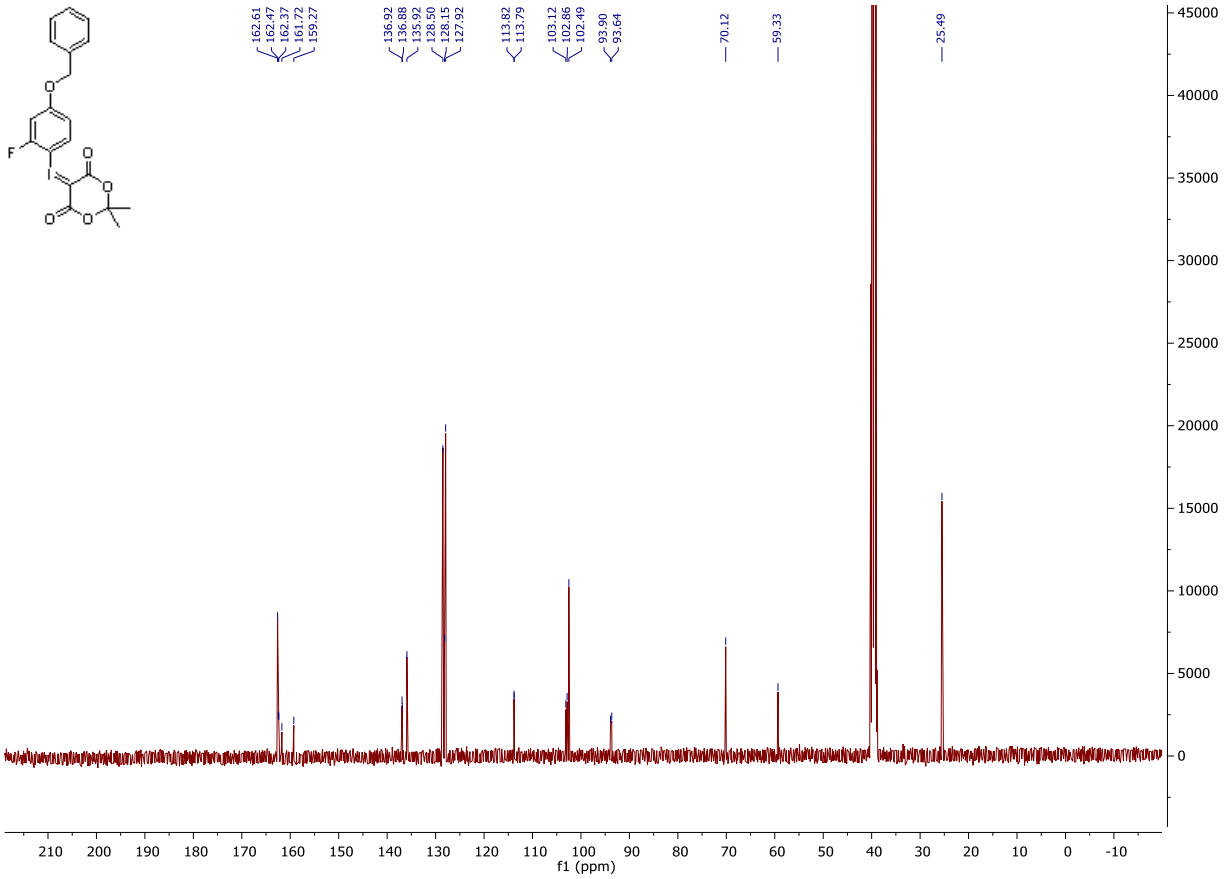
5-((4-methoxyphenyl)-l3-iodaneylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione



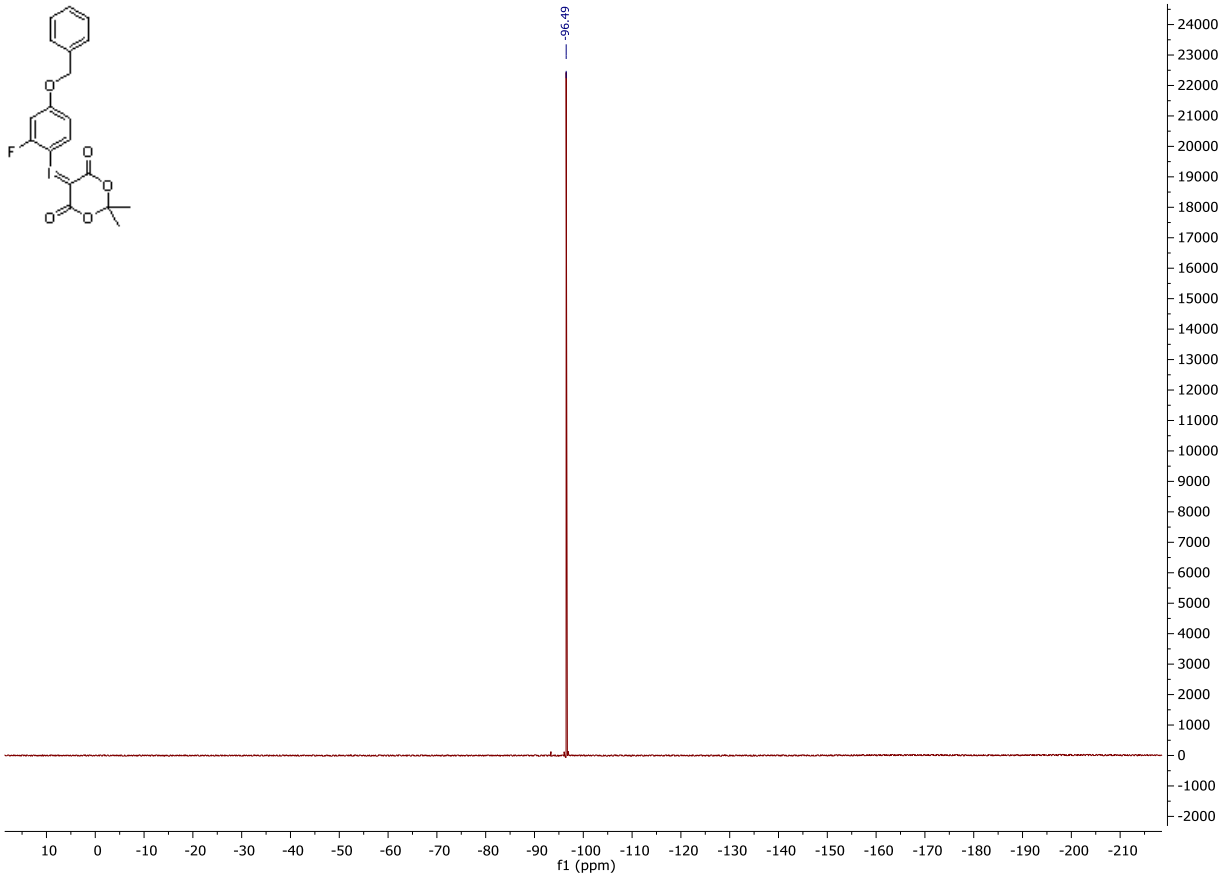
5-((4-(benzyloxy)-2-fluorophenyl)-l3-iodaneylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione



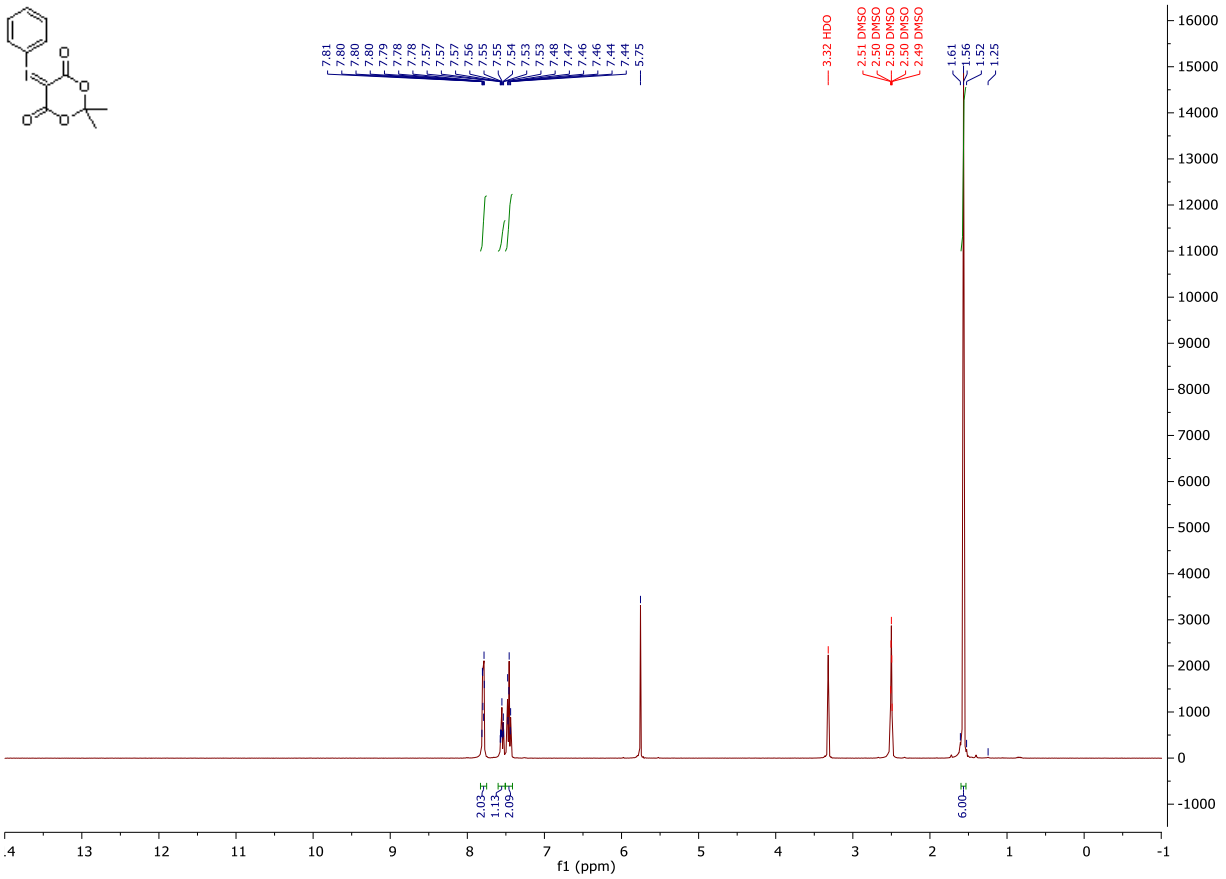
5-((4-(benzyloxy)-2-fluorophenyl)-l3-iodaneylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione



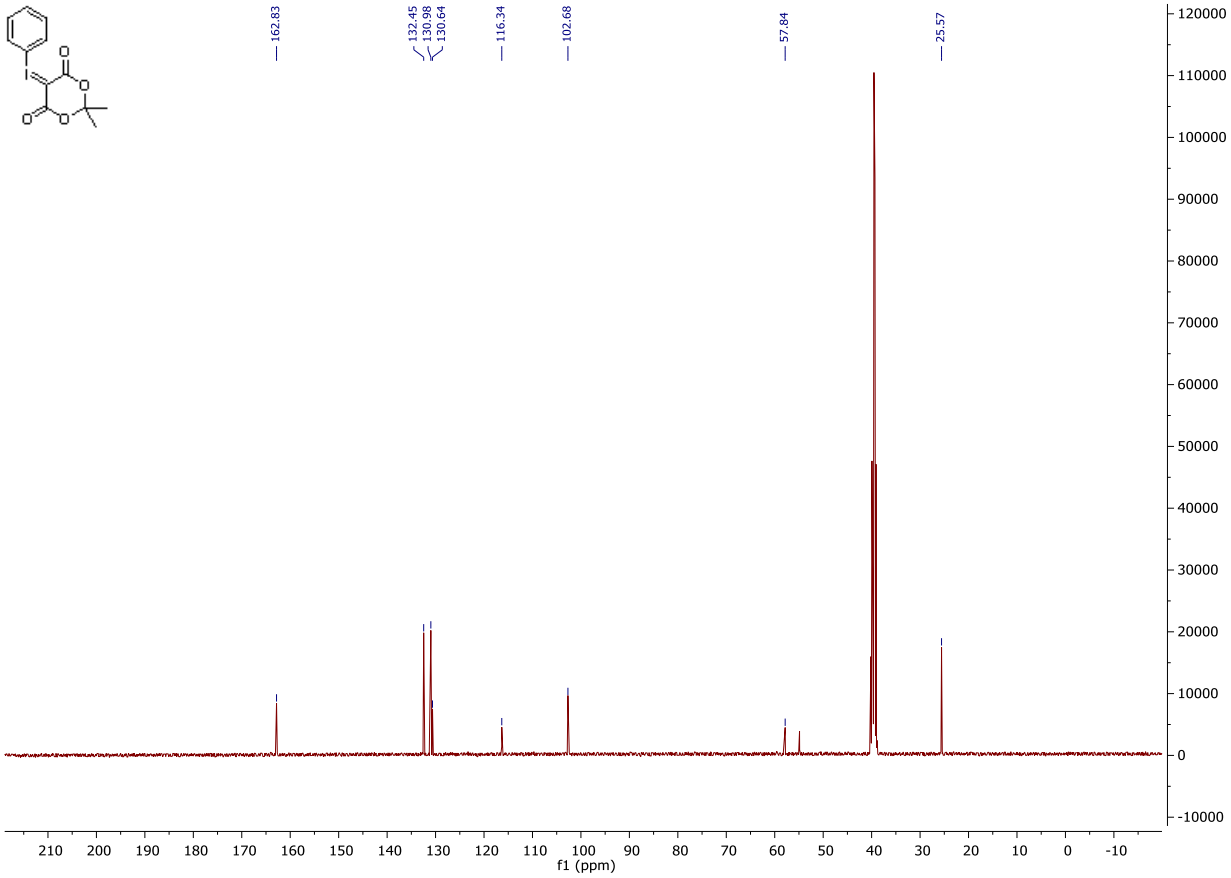
5-((4-(benzyloxy)-2-fluorophenyl)-l3-iodaneylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione



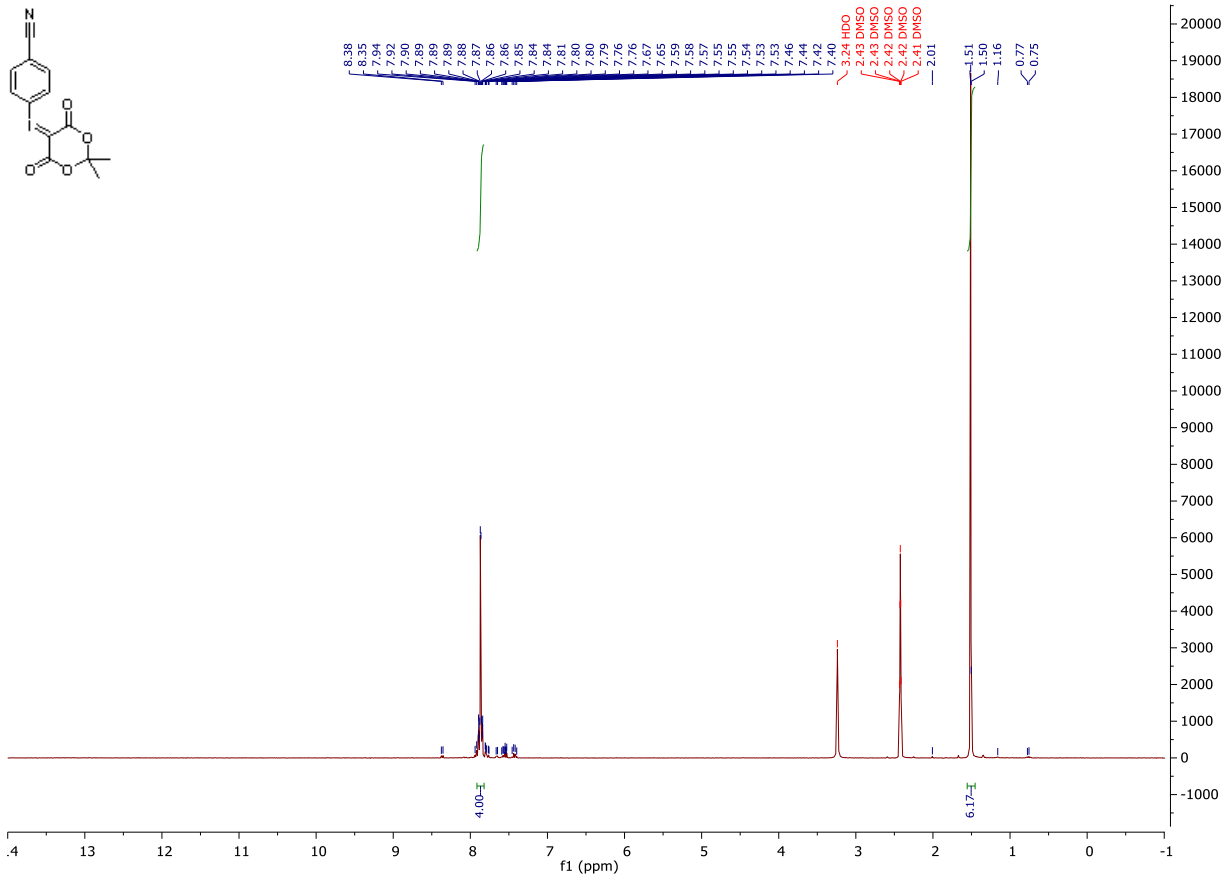
2,2-dimethyl-5-(phenyl-l3-iodaneylidene)-1,3-dioxane-4,6-dione



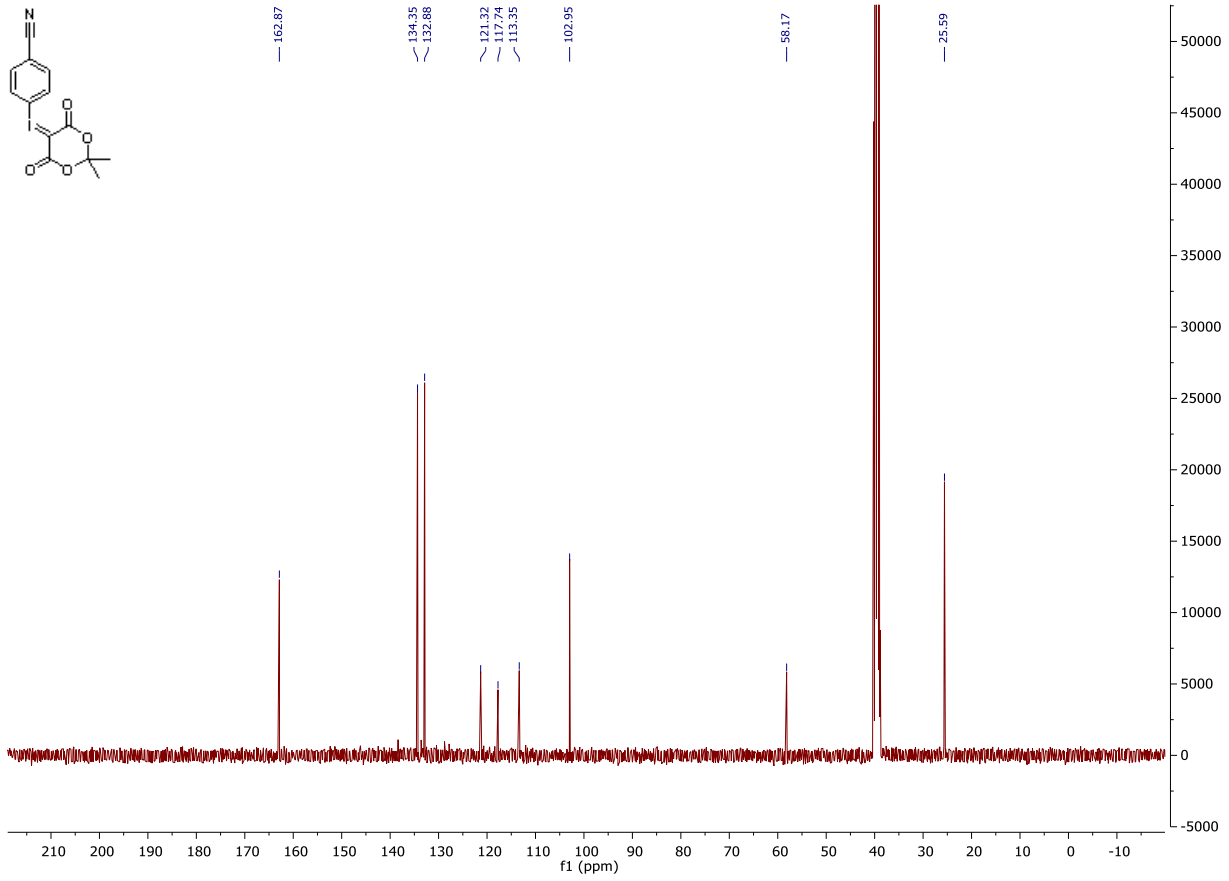
2,2-dimethyl-5-(phenyl-l3-iodaneylidene)-1,3-dioxane-4,6-dione



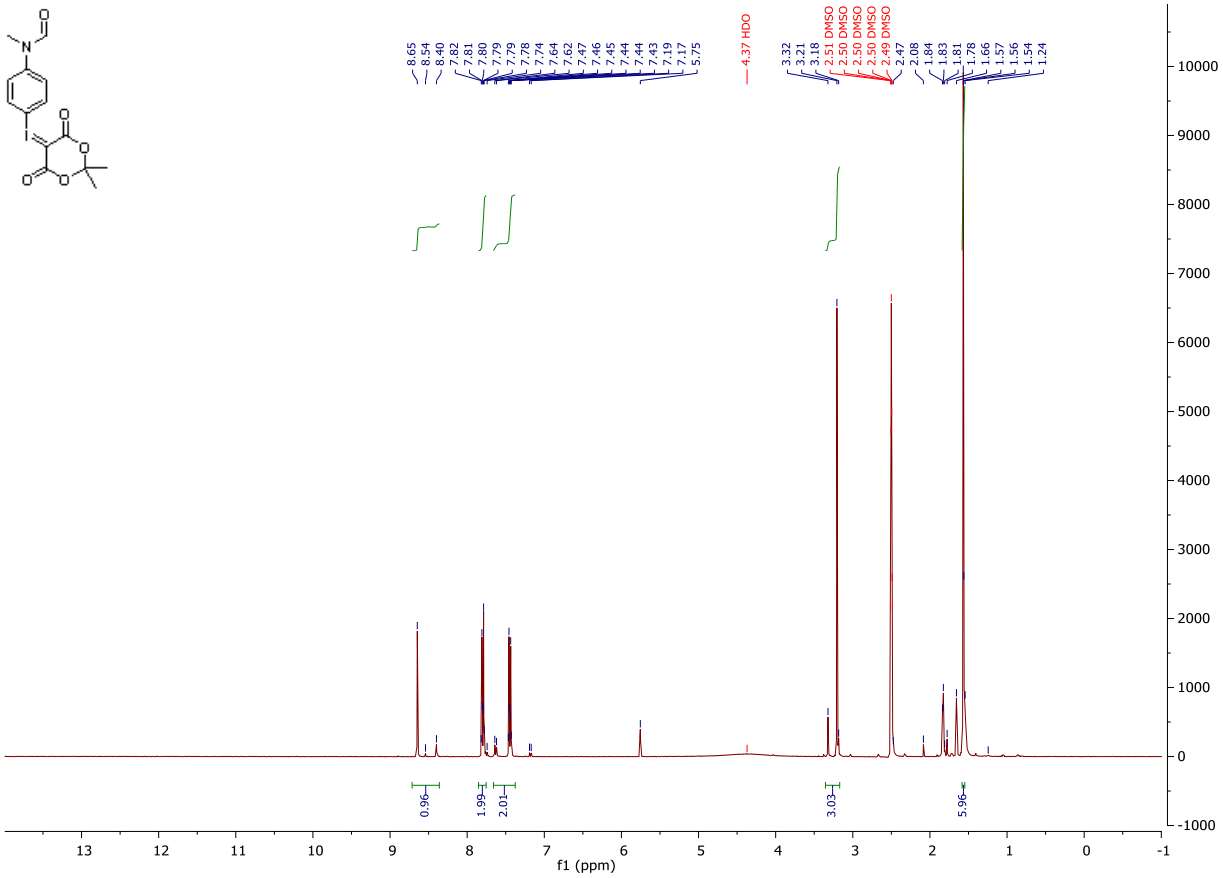
4-((2,2-dimethyl-4,6-dioxo-1,3-dioxan-5-ylidene)-l3-iodaneyl)benzonitrile



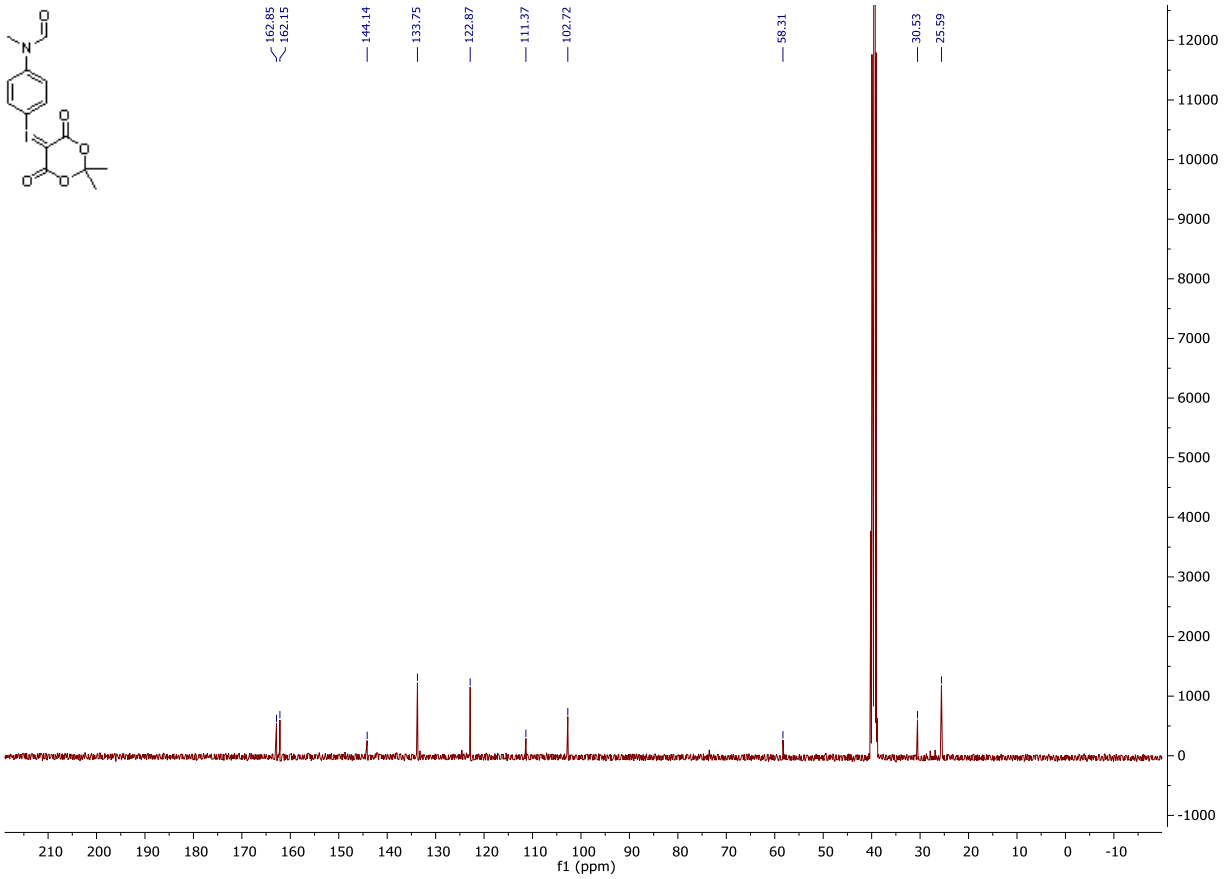
4-((2,2-dimethyl-4,6-dioxo-1,3-dioxan-5-ylidene)-l3-iodaneyl)benzonitrile



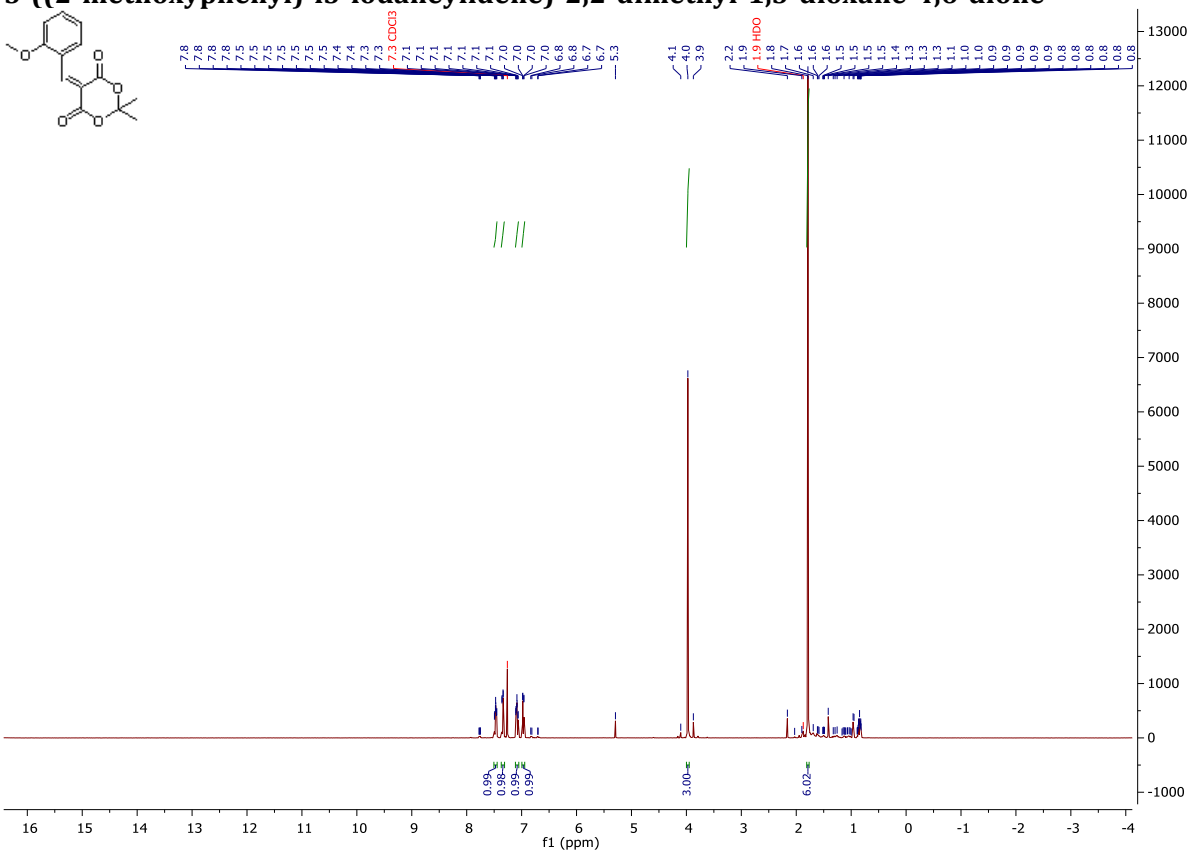
N-(4-((2,2-dimethyl-4,6-dioxo-1,3-dioxan-5-ylidene)-l3-iodaneyl)phenyl)-N-methylformamide



N-(4-((2,2-dimethyl-4,6-dioxo-1,3-dioxan-5-ylidene)-l3-iodaneyl)phenyl)-N-methylformamide

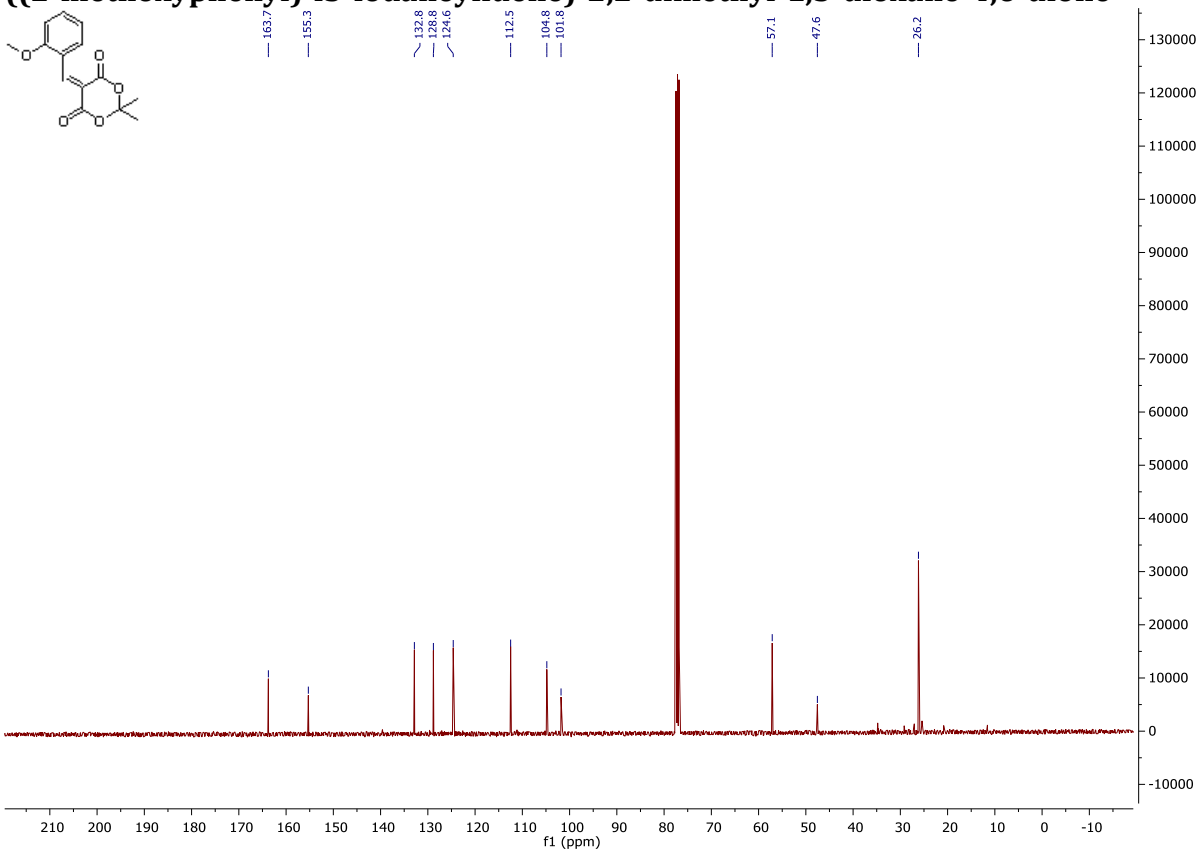


5-((2-methoxyphenyl)-l3-iodaneylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione

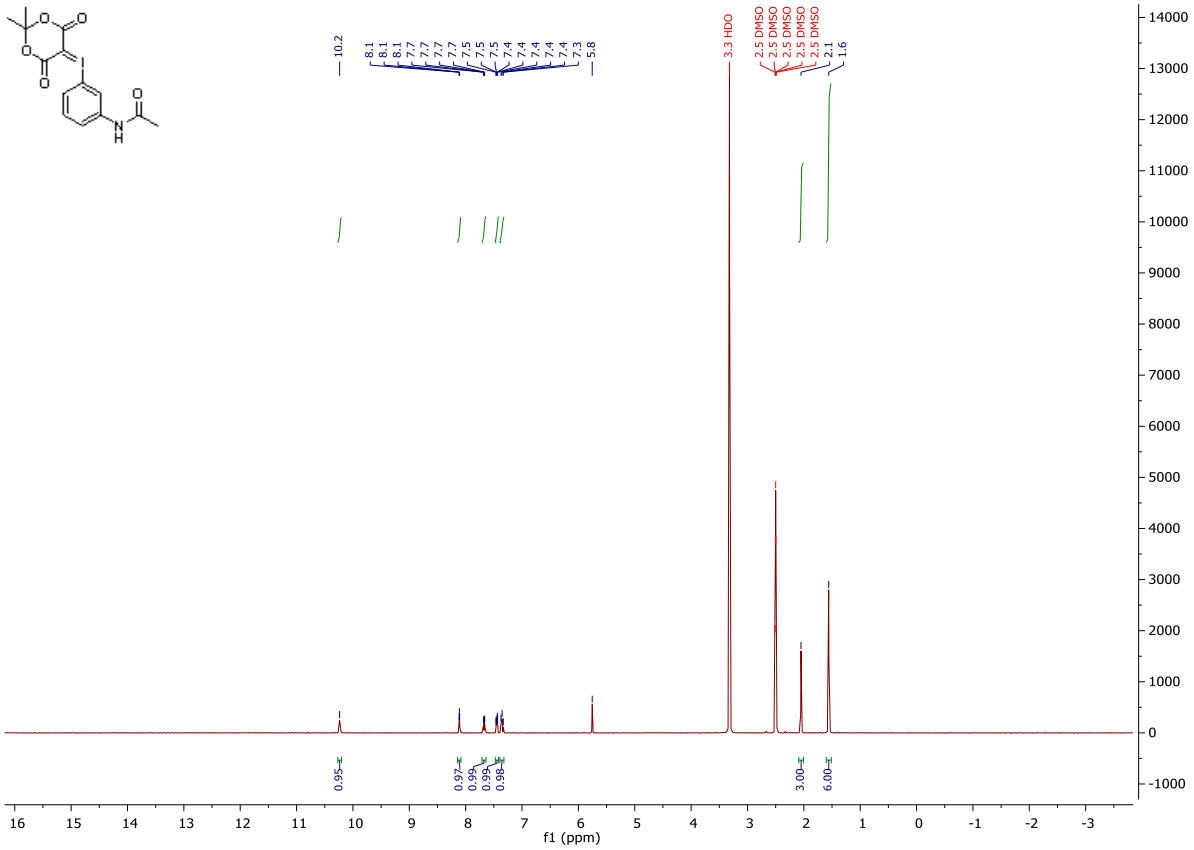


5-

((2-methoxyphenyl)-l3-iodaneylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione

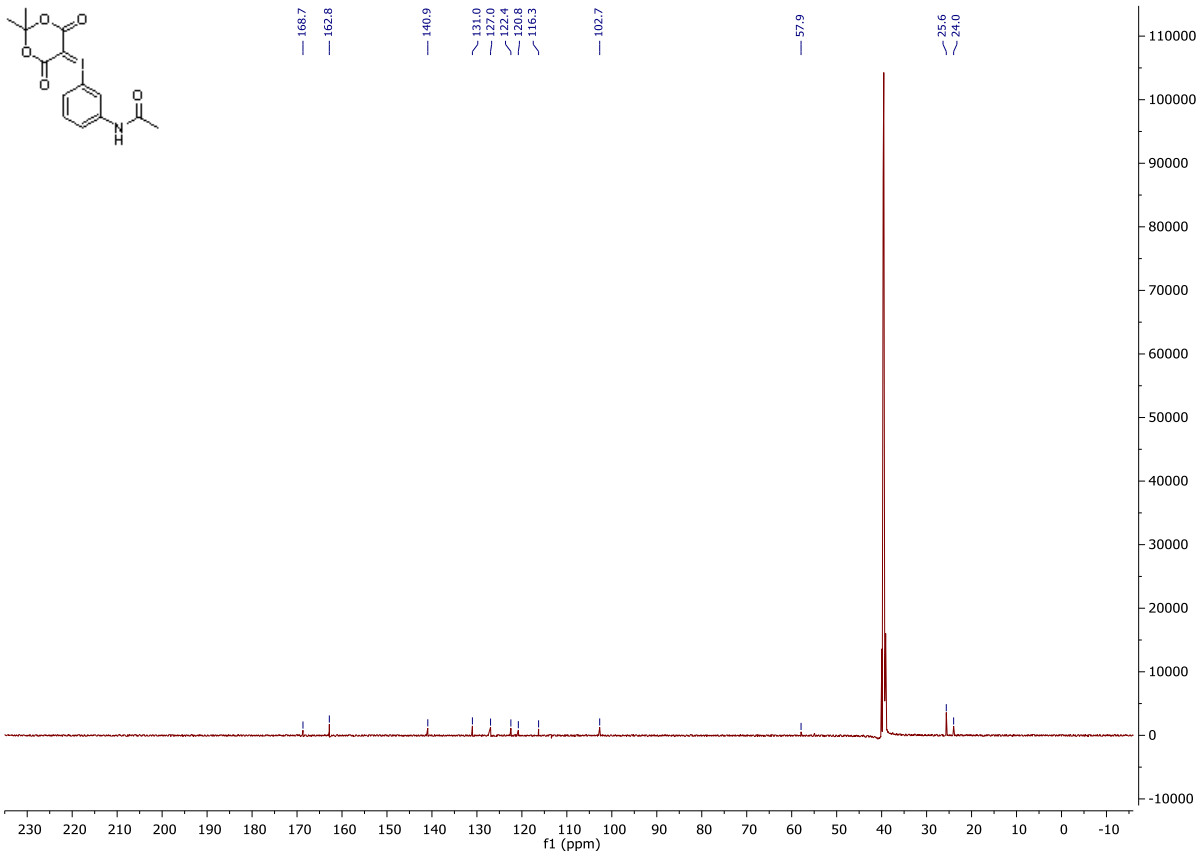


N-(3-((2,2-dimethyl-4,6-dioxo-1,3-dioxan-5-ylidene)-l3-iodaneyl)phenyl)acetamide

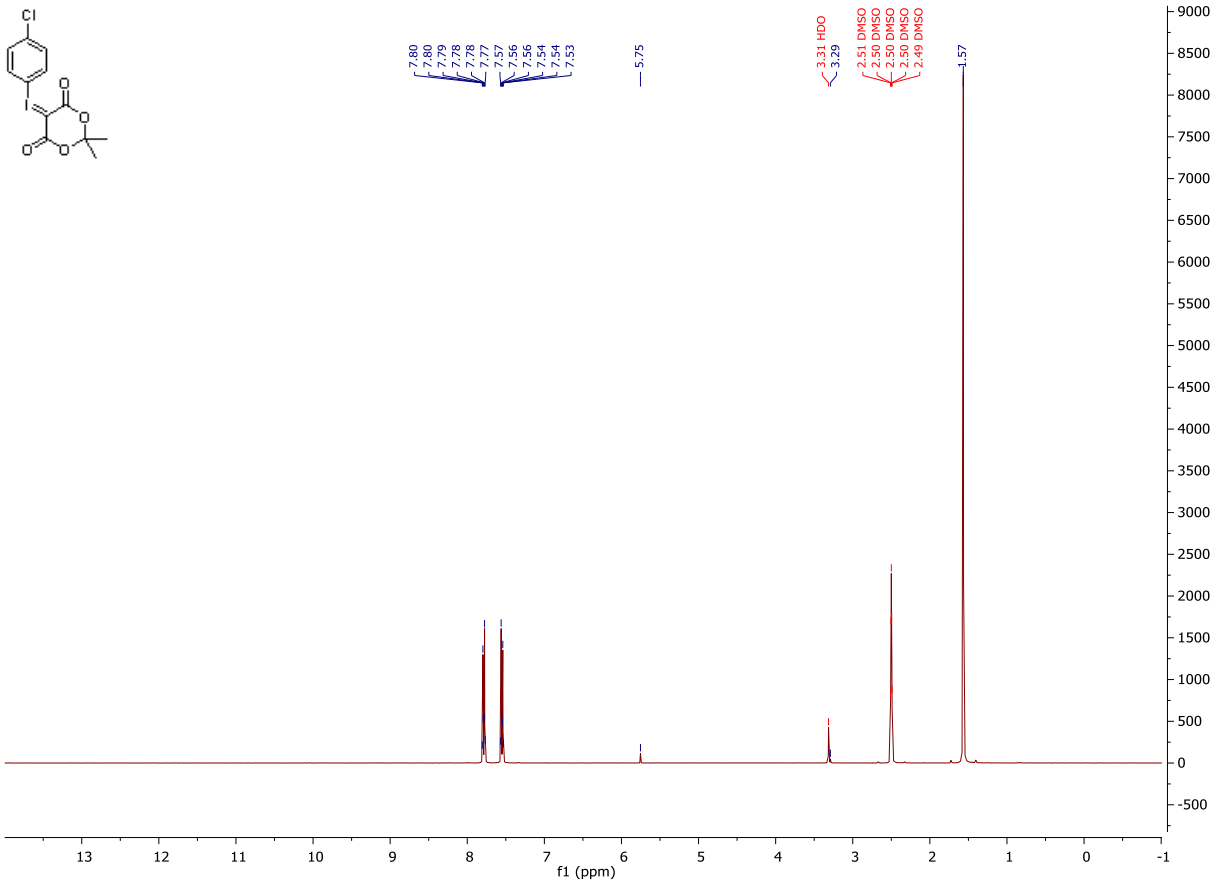


N-

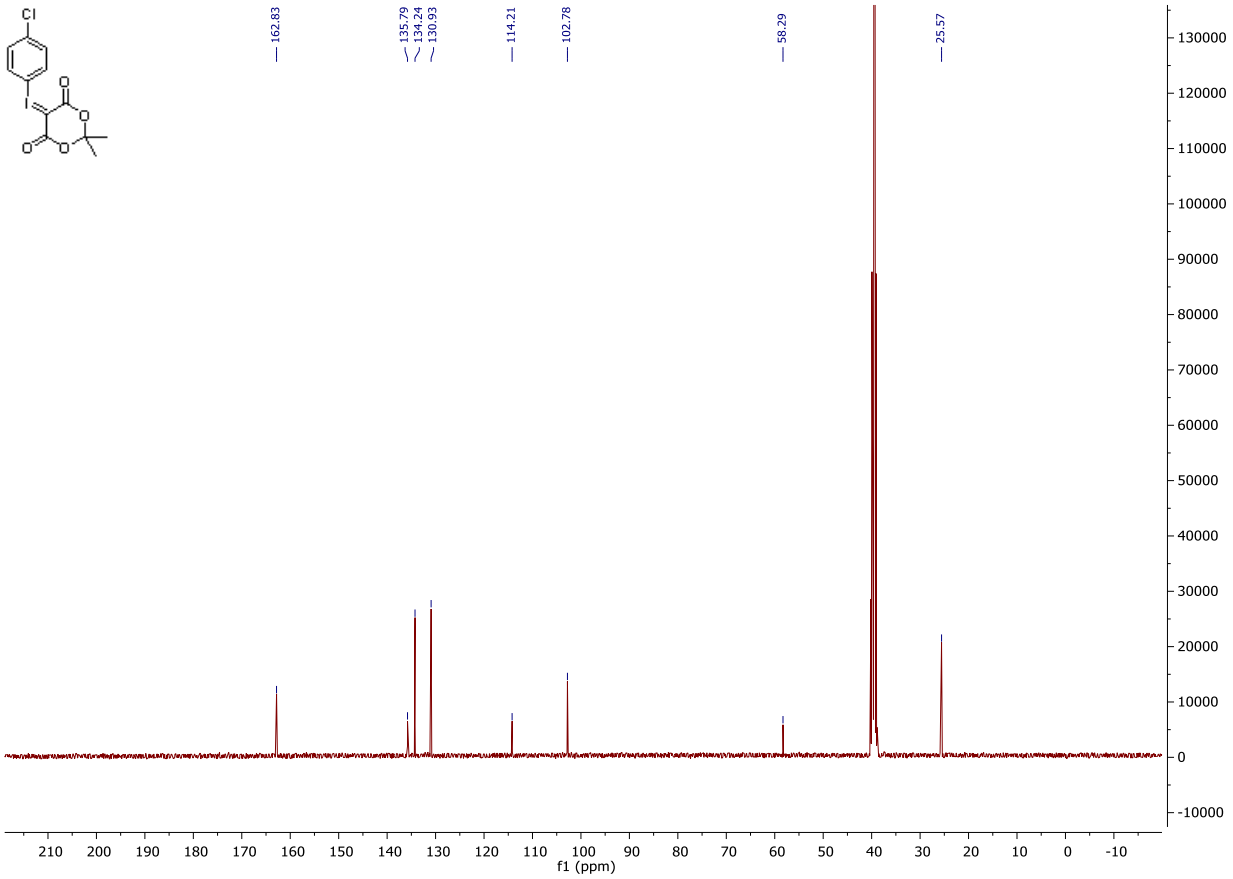
(3-((2,2-dimethyl-4,6-dioxo-1,3-dioxan-5-ylidene)-l3-iodaneyl)phenyl)acetamide



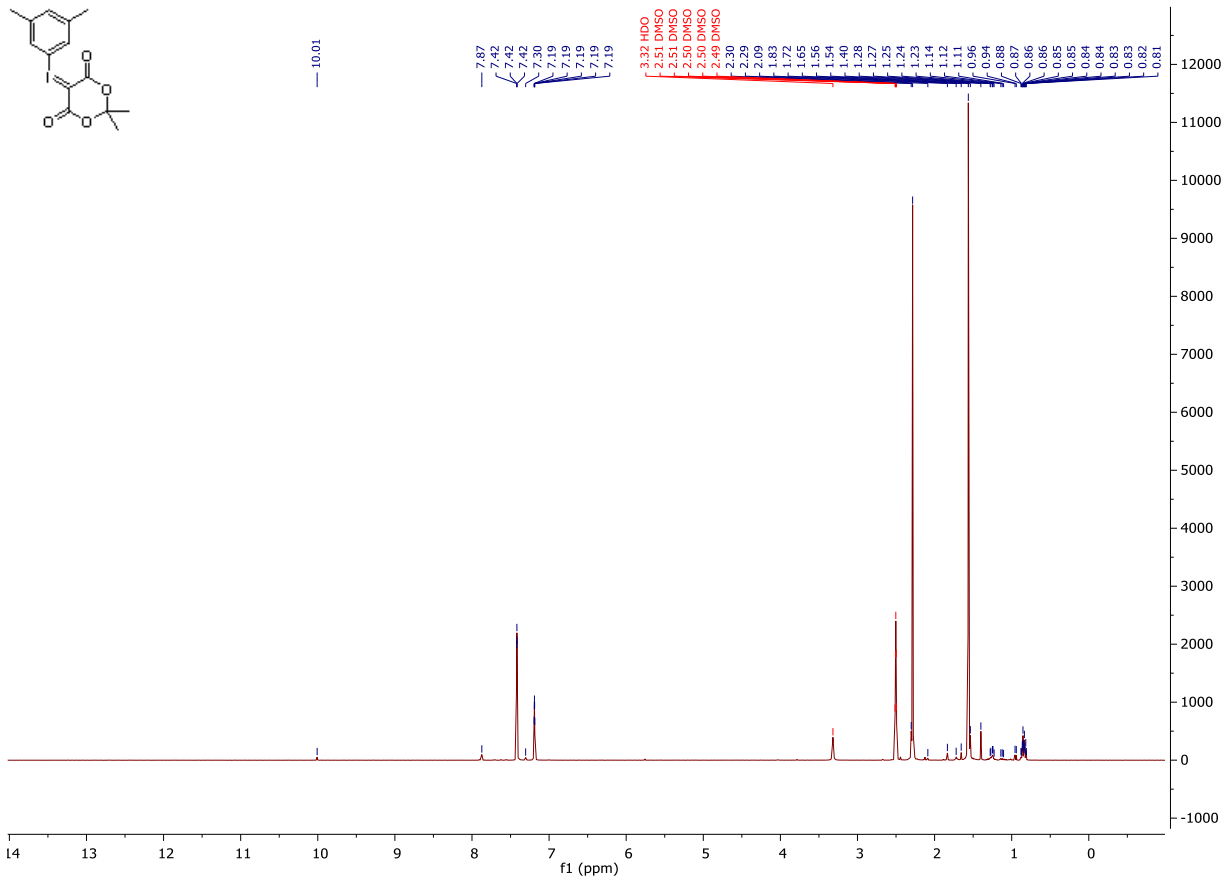
5-((4-chlorophenyl)-l3-iodaneylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione



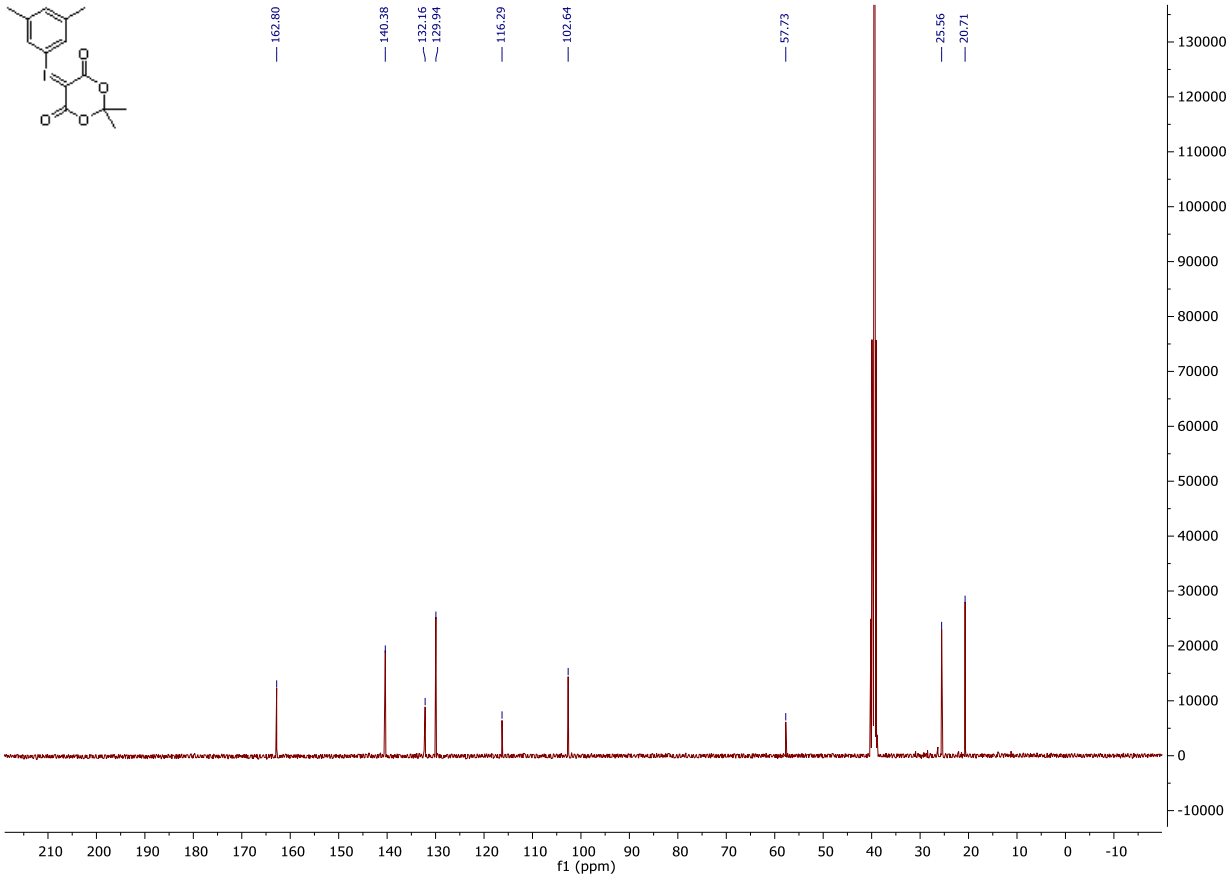
5-((4-chlorophenyl)-l3-iodaneylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione



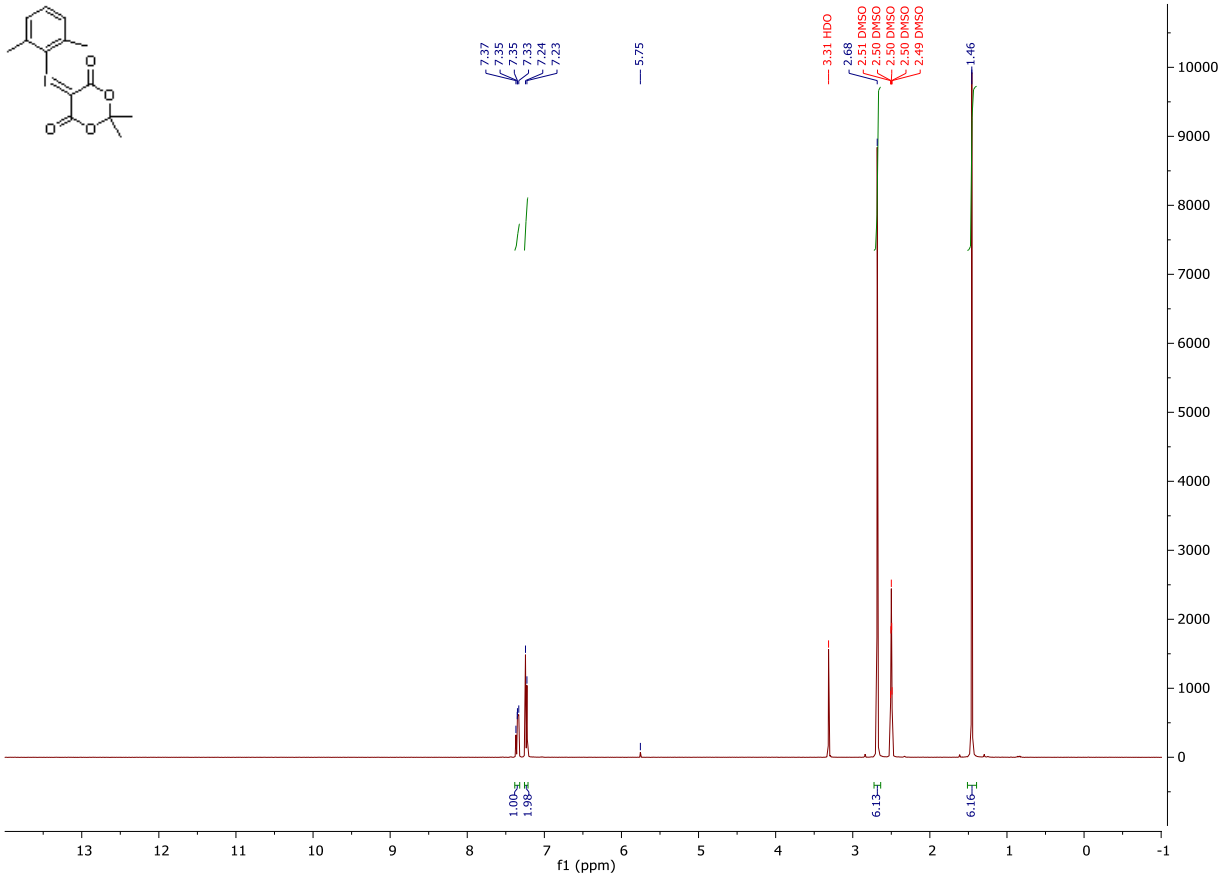
5-((3,5-dimethylphenyl)-l3-iodaneylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione



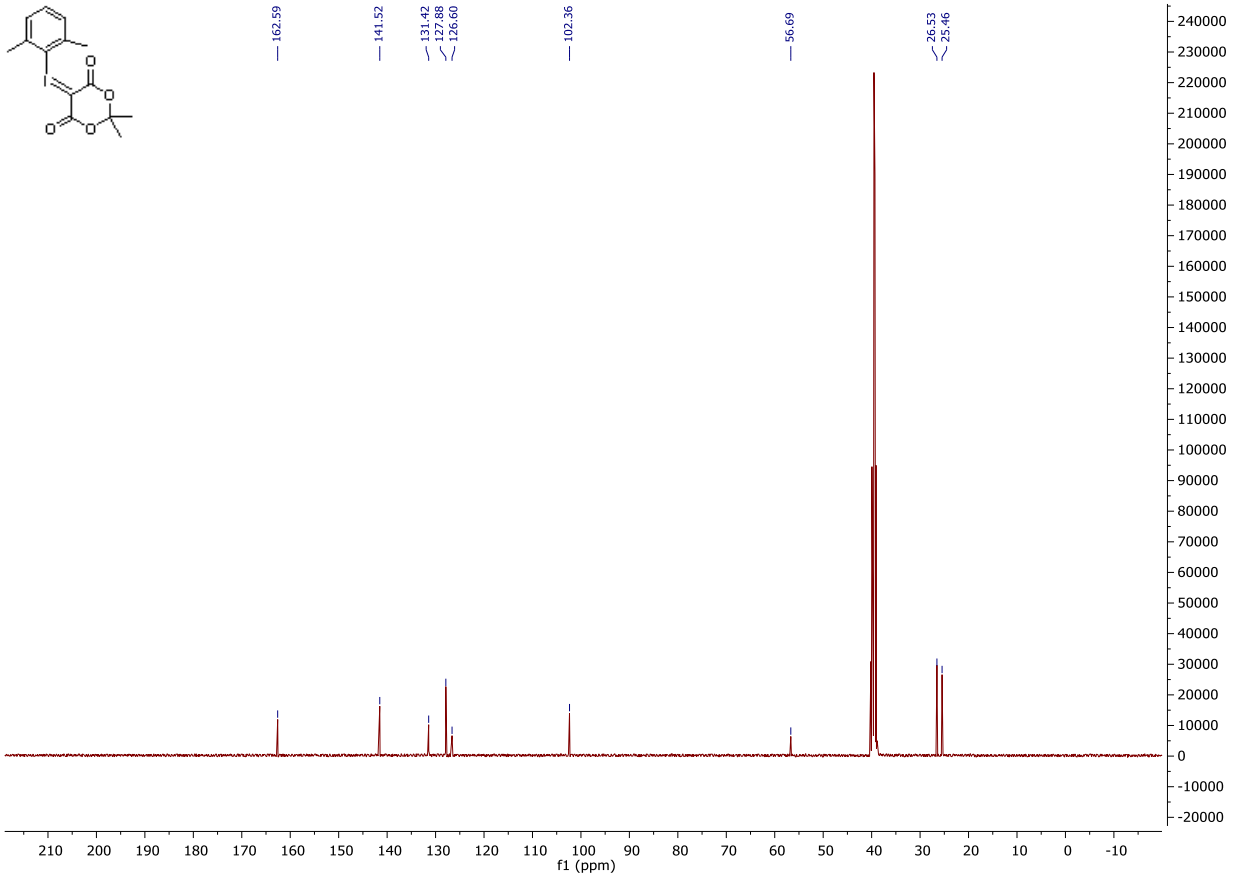
5-((3,5-dimethylphenyl)-l3-iodaneylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione



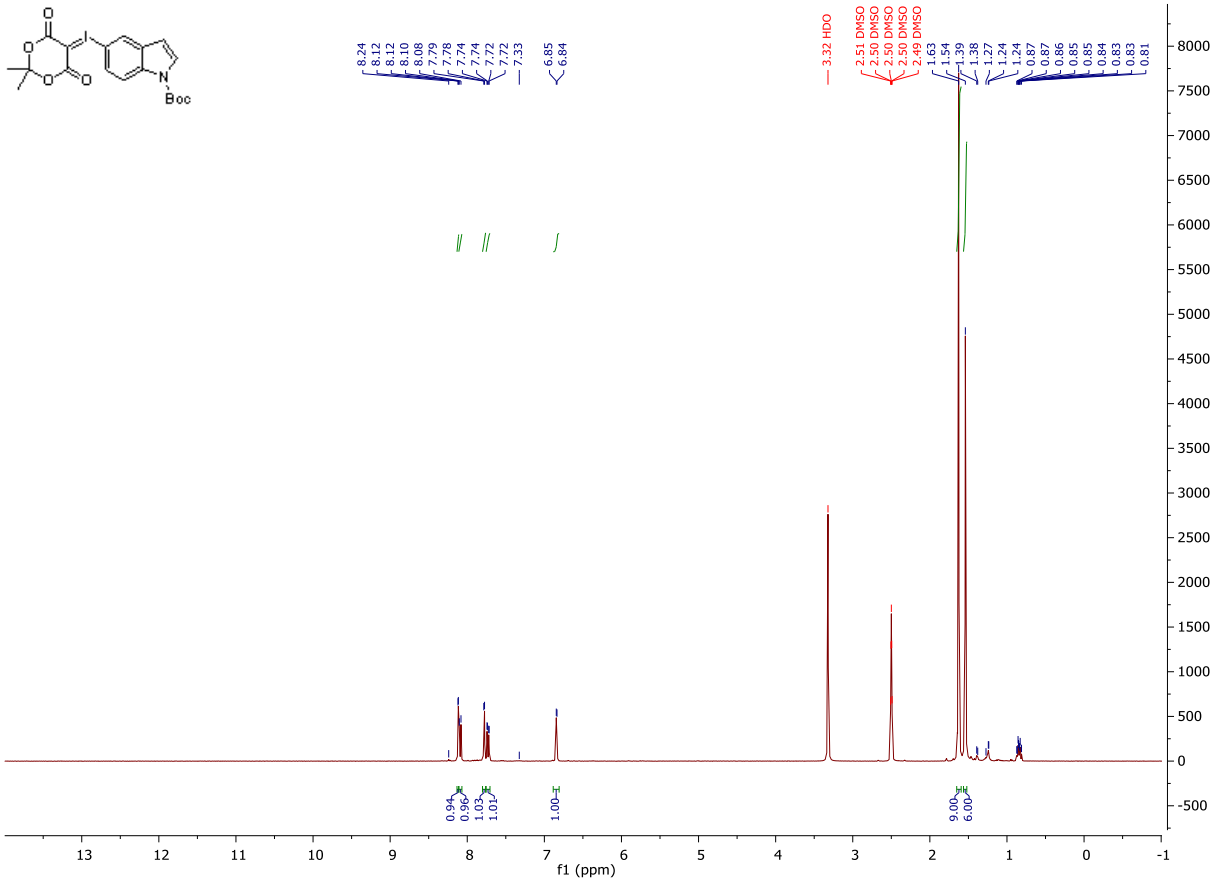
5-((2,6-dimethylphenyl)-l3-iodaneylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione



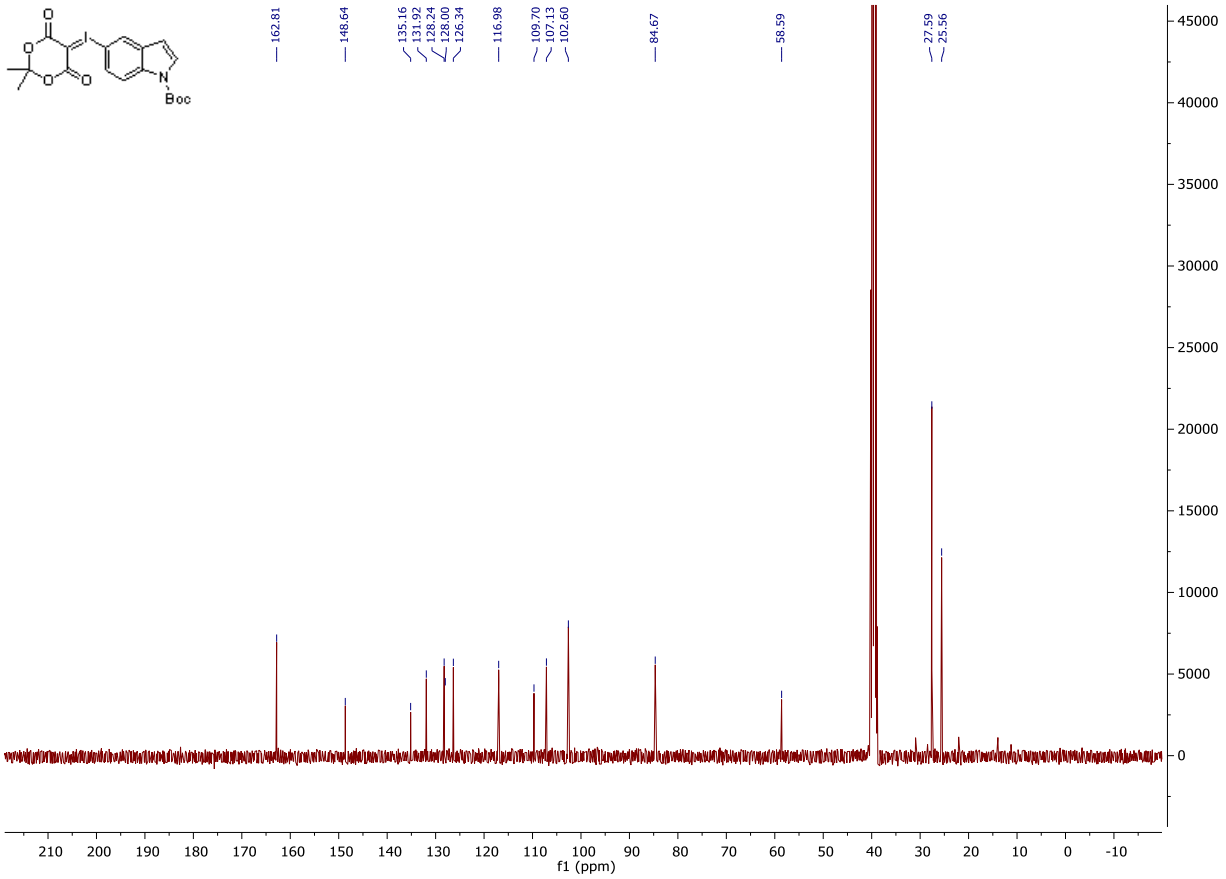
5-((2,6-dimethylphenyl)-l3-iodaneylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione



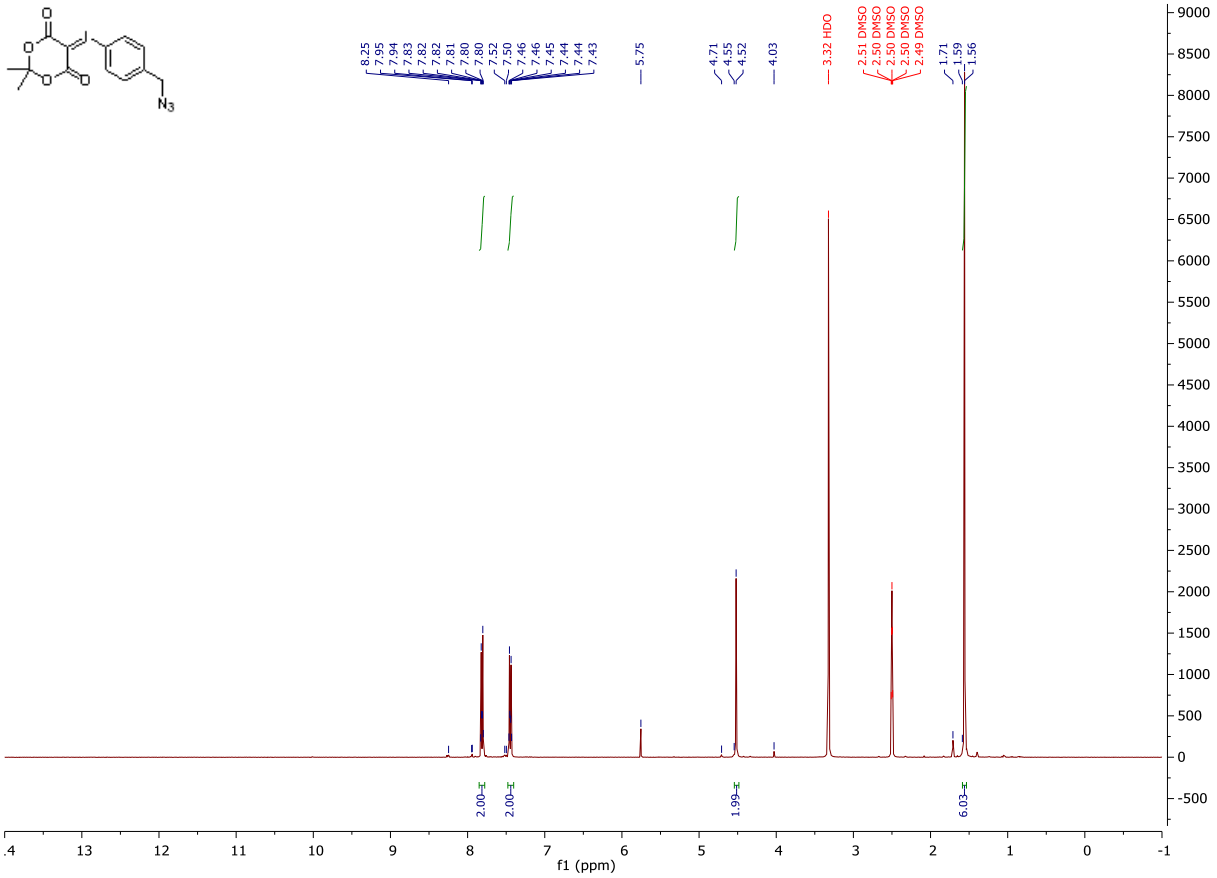
tert-butyl 5-((2,2-dimethyl-4,6-dioxo-1,3-dioxan-5-ylidene)-l3-iodaneyl)-1H-indole-1-carboxylate



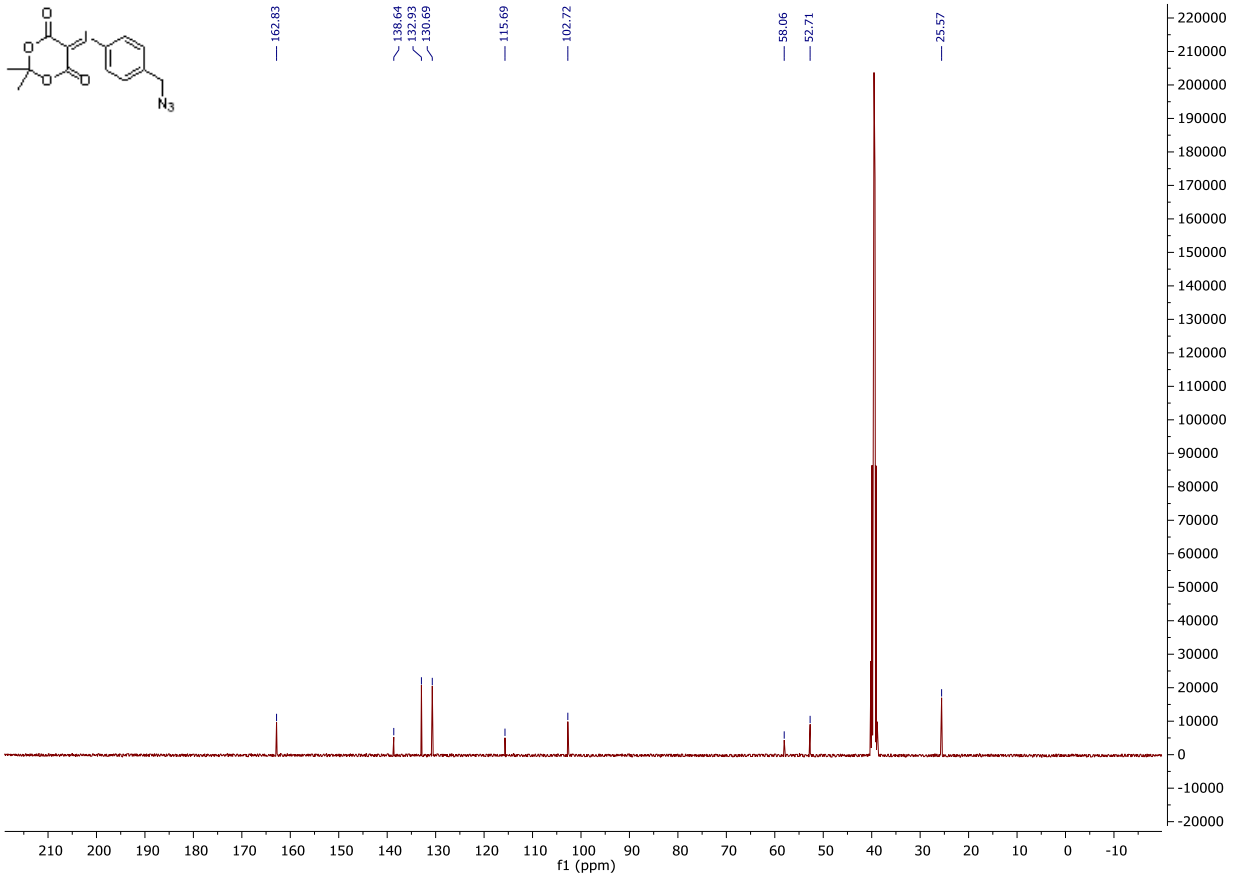
tert-butyl 5-((2,2-dimethyl-4,6-dioxo-1,3-dioxan-5-ylidene)-l3-iodaneyl)-1H-indole-1-carboxylate



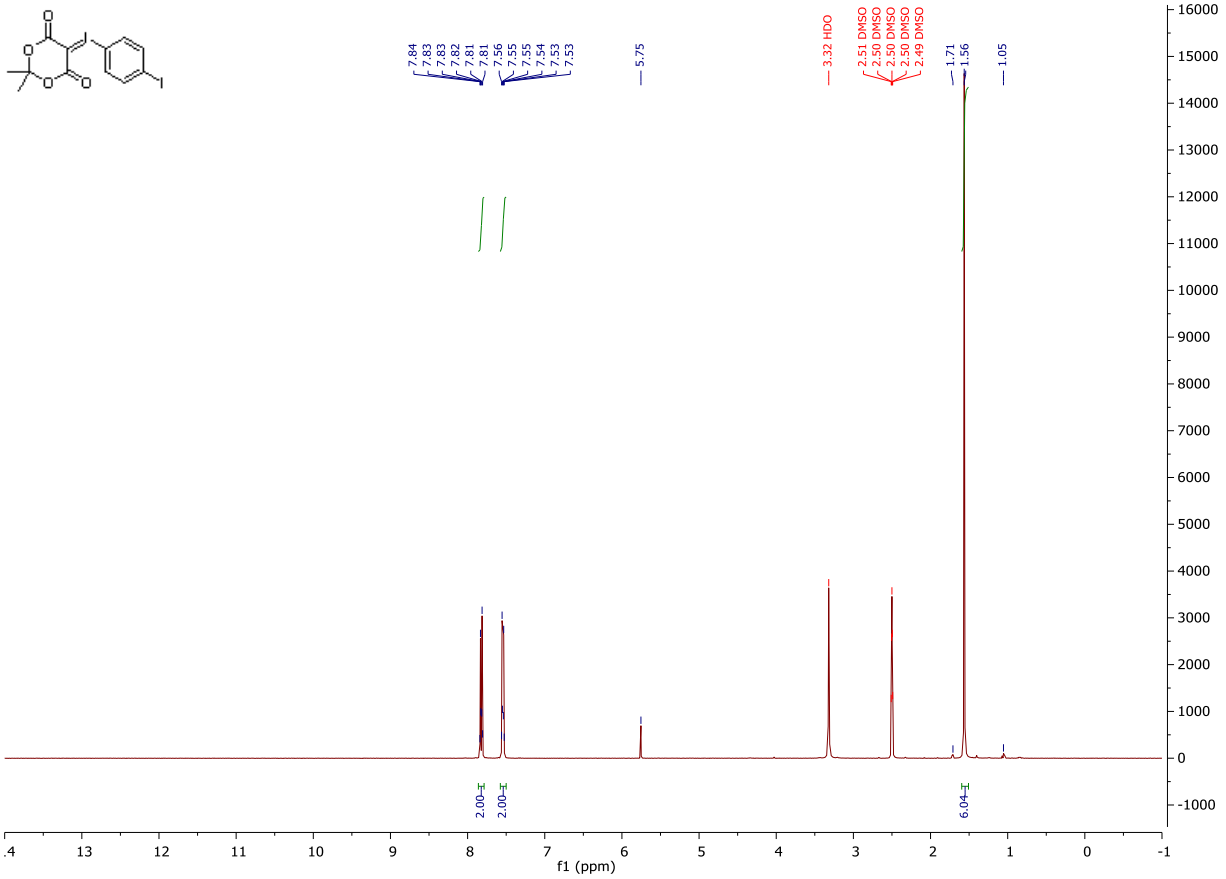
5-((4-(azidomethyl)phenyl)-l3-iodaneylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione



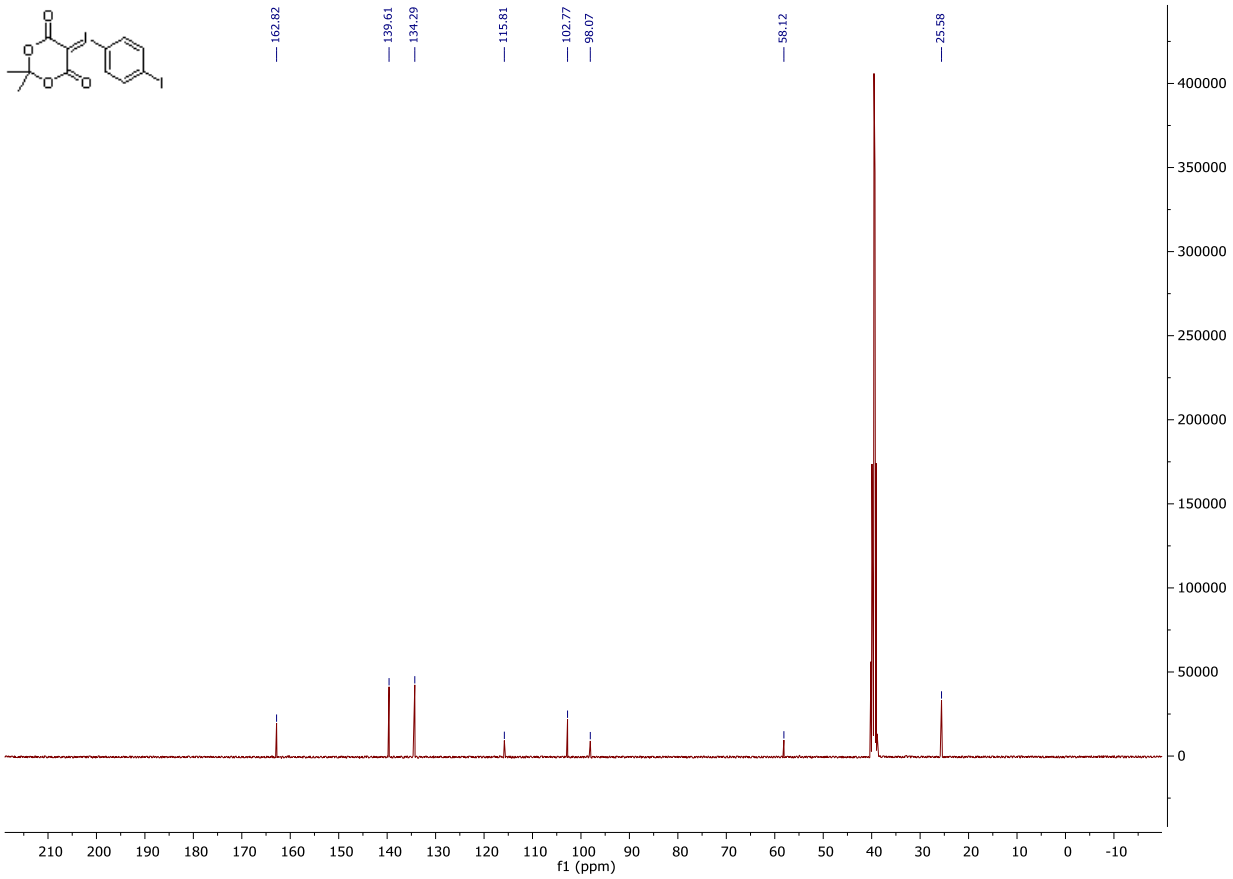
5-((4-(azidomethyl)phenyl)-l3-iodaneylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione



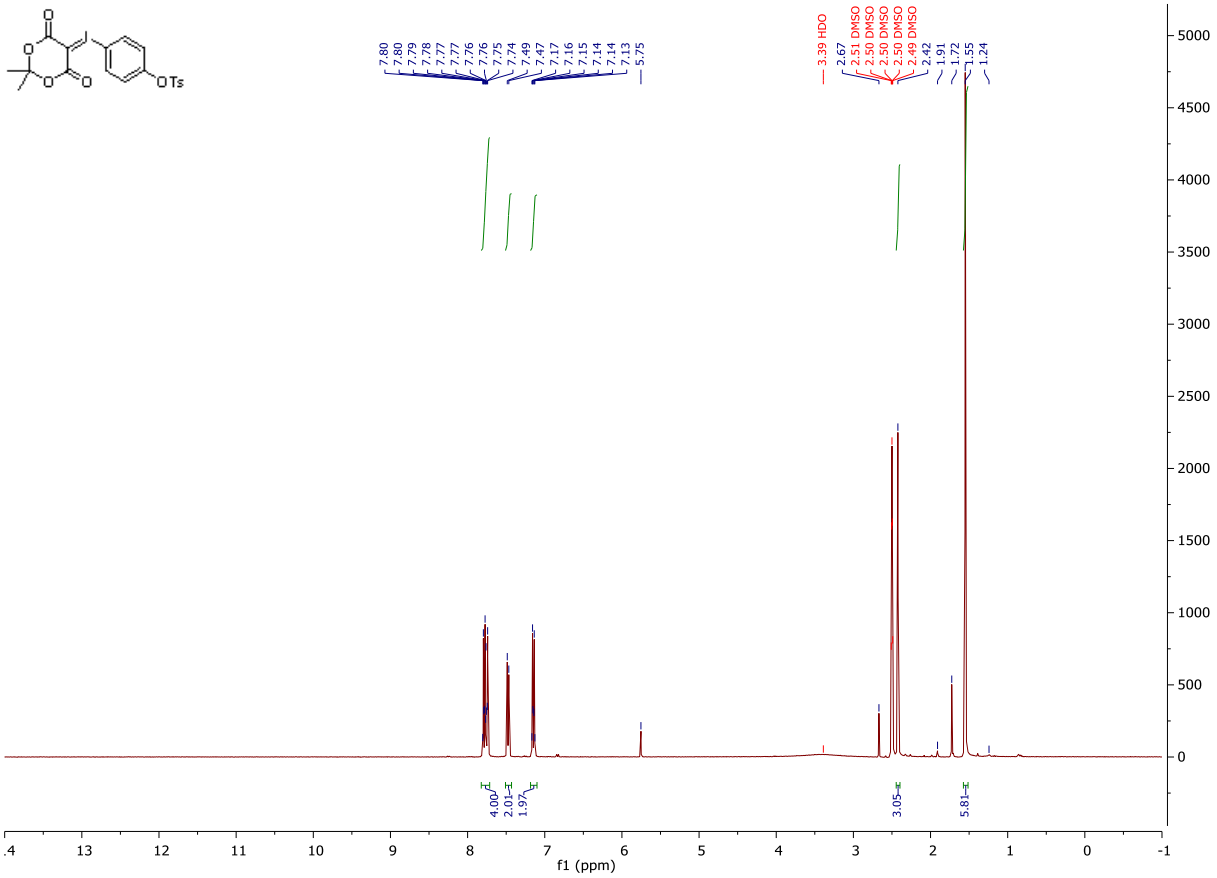
5-((4-iodophenyl)-l3-iodaneylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione



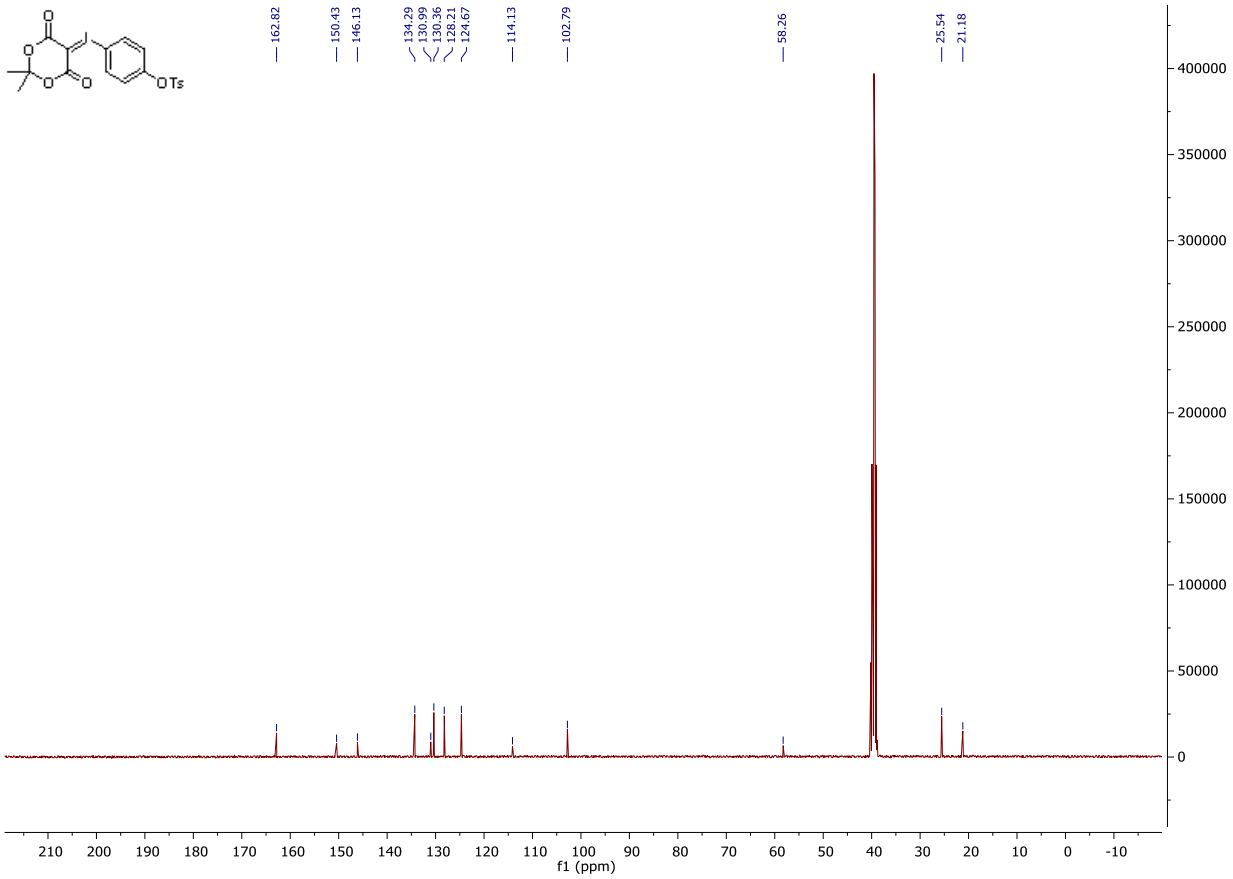
5-((4-iodophenyl)-l3-iodaneylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione



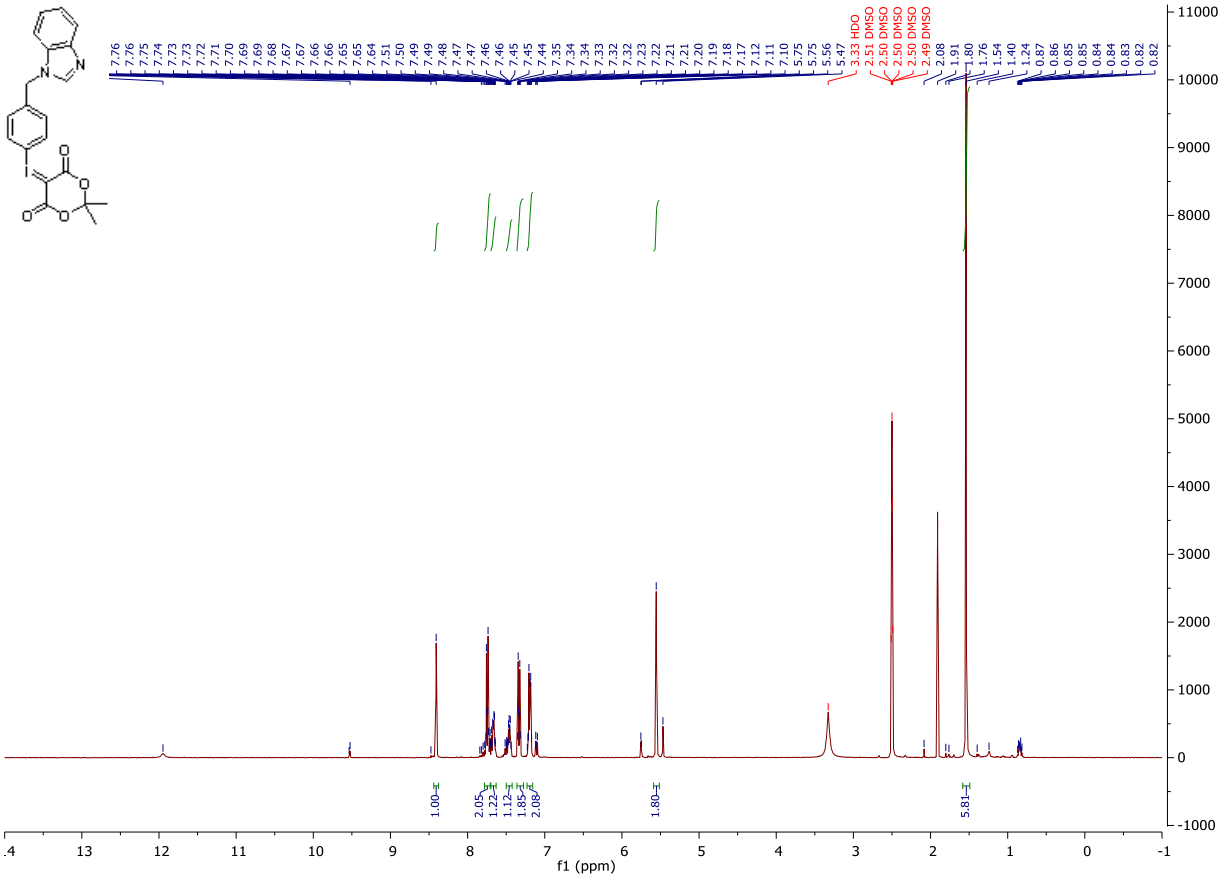
4-((2,2-dimethyl-4,6-dioxo-1,3-dioxan-5-ylidene)-l3-iodaneyl)phenyl 4-methylbenzenesulfonate



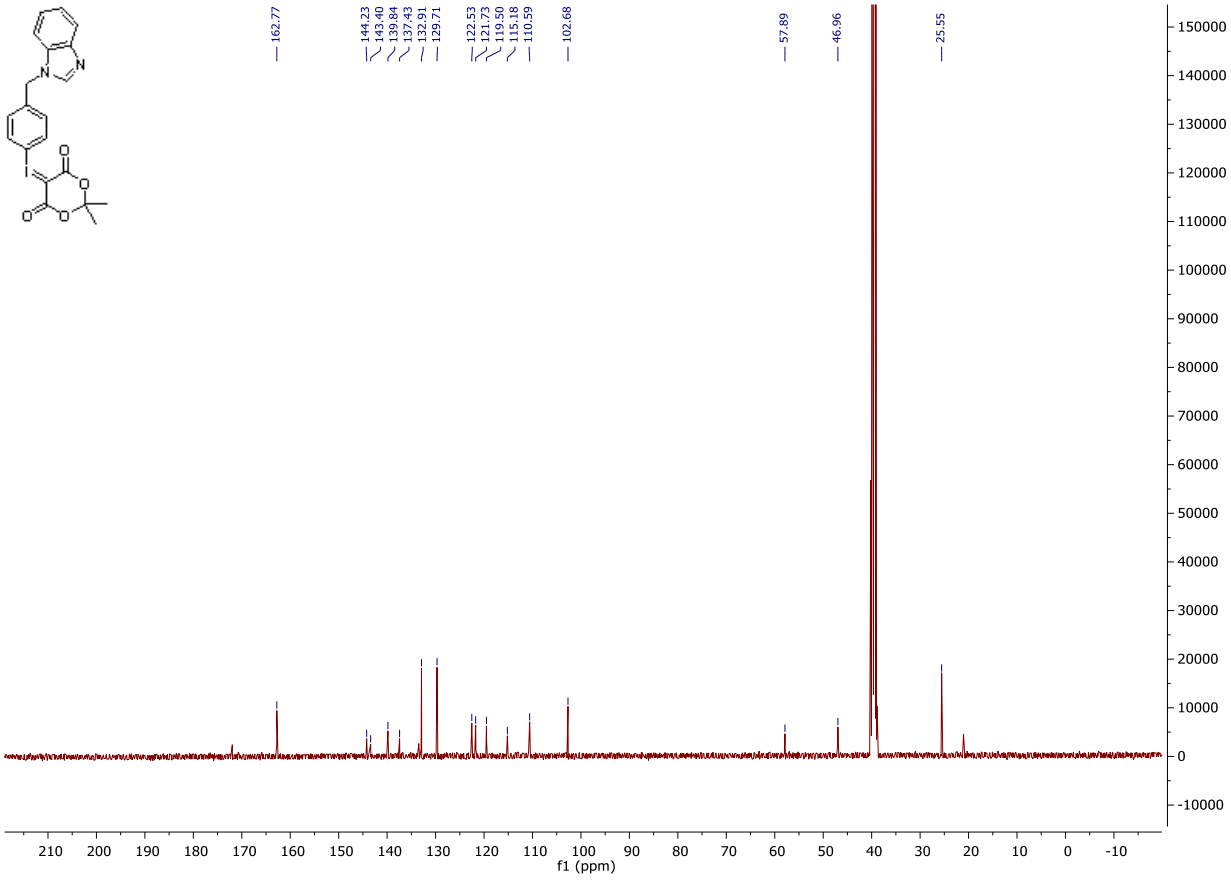
4-((2,2-dimethyl-4,6-dioxo-1,3-dioxan-5-ylidene)-l3-iodaneyl)phenyl 4-methylbenzenesulfonate



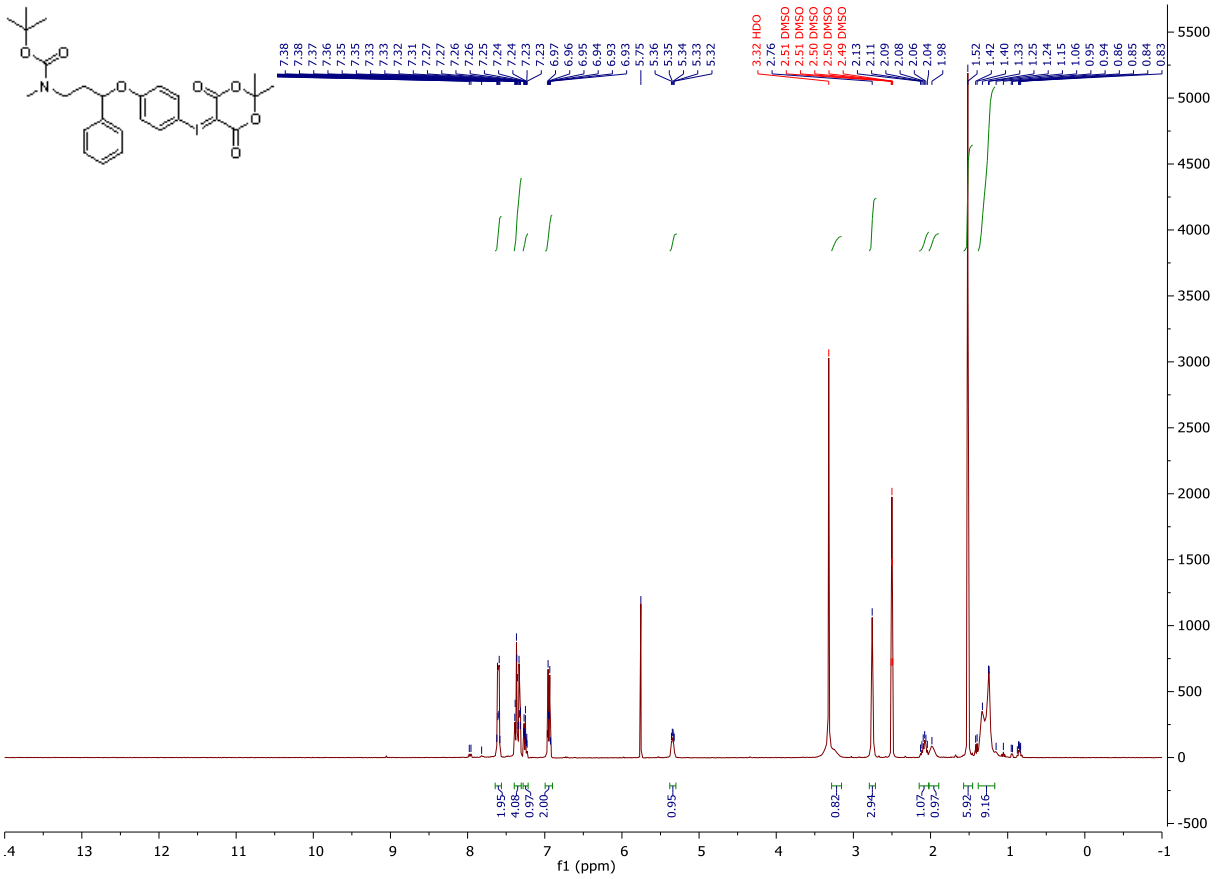
5-((4-((1H-benzo[d]imidazol-1-yl)methyl)phenyl)-l3-iodaneylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione



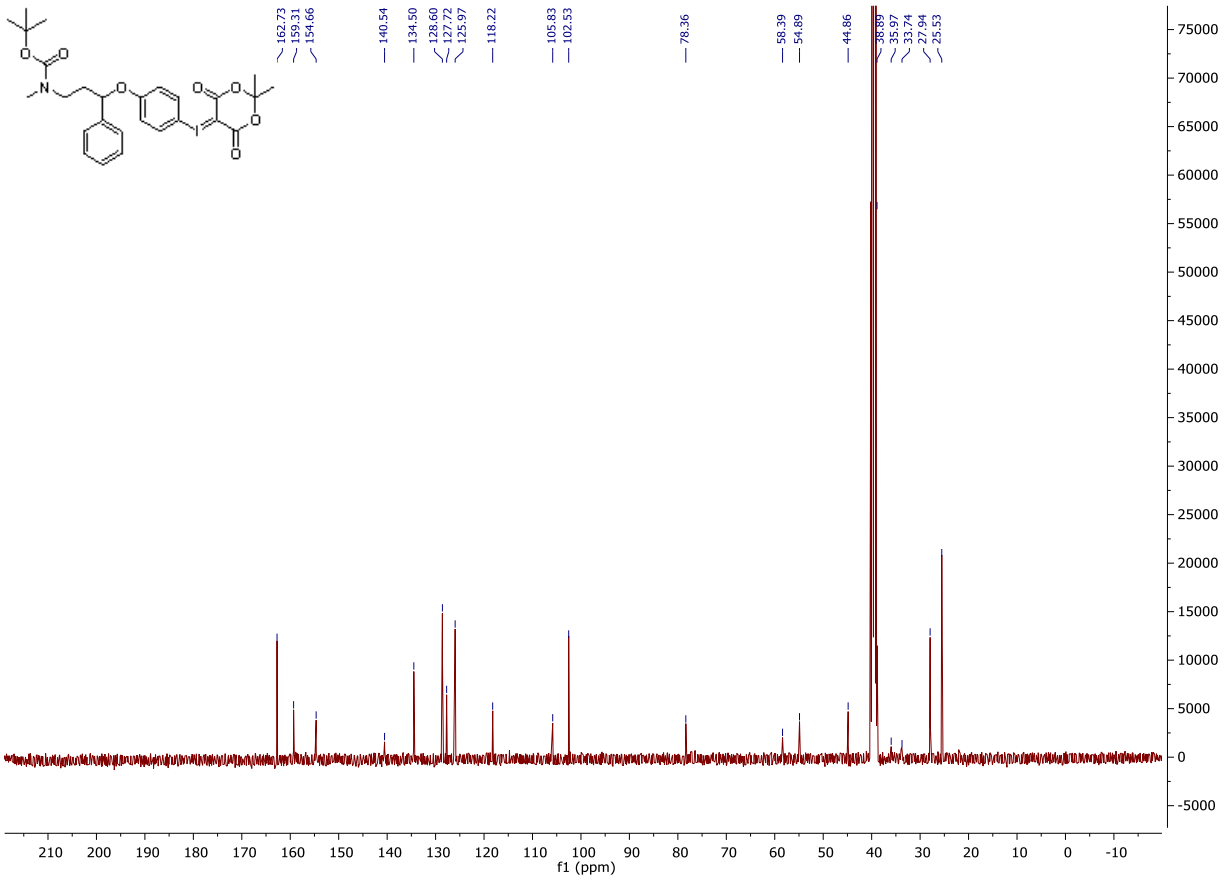
5-((4-((1H-benzo[d]imidazol-1-yl)methyl)phenyl)-l3-iodaneylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione



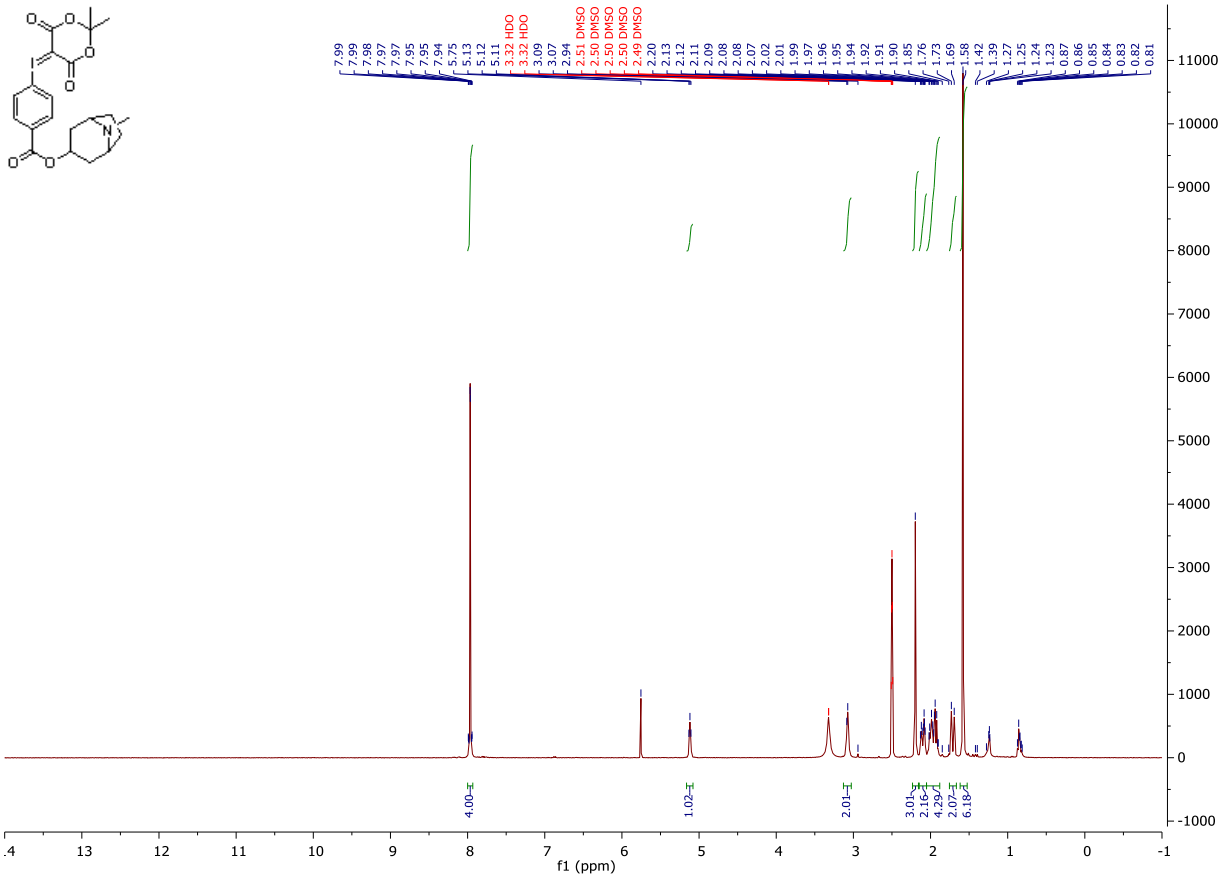
tert-butyl (3-(4-((2,2-dimethyl-4,6-dioxo-1,3-dioxan-5-ylidene)-l3-iodaneyl)phenoxy)-3-phenylpropyl)(methyl)carbamate



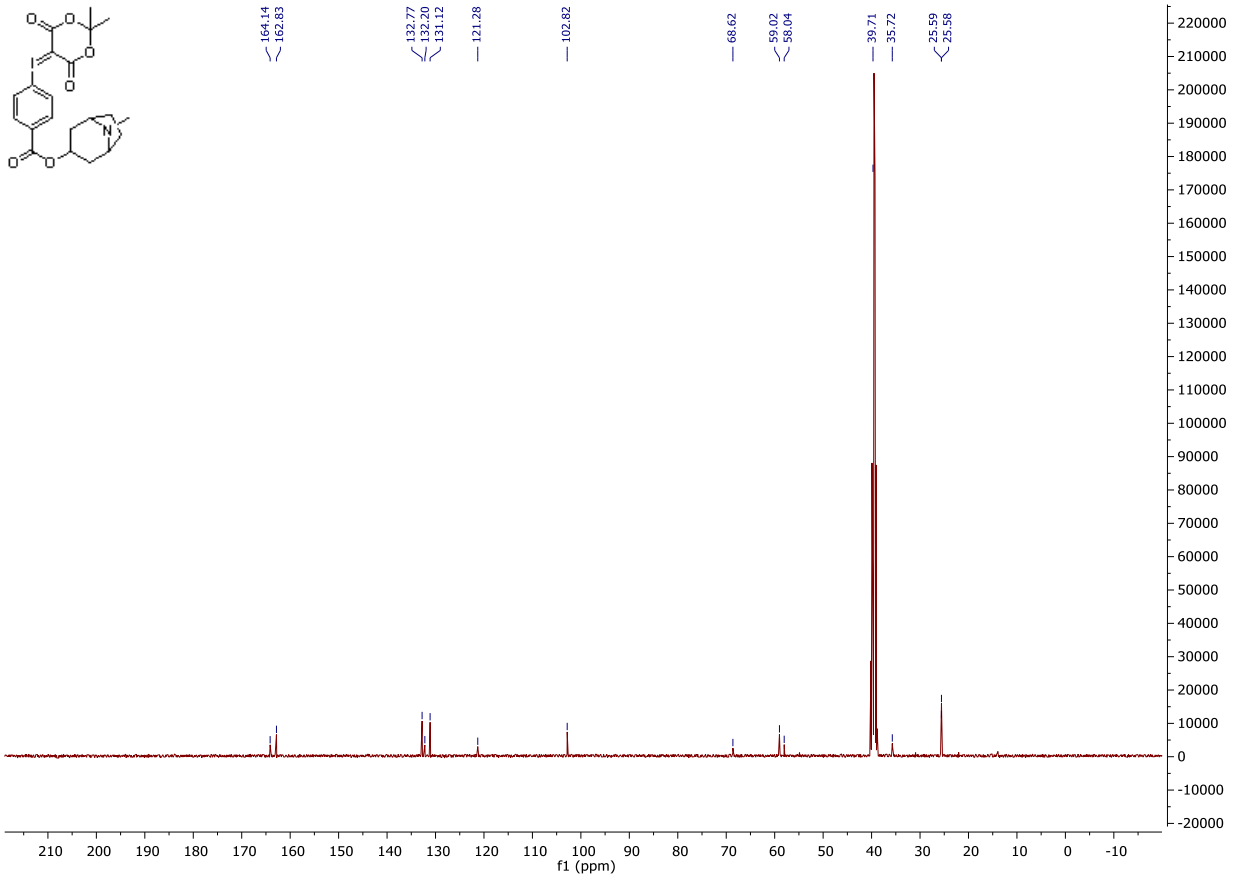
tert-butyl (3-(4-((2,2-dimethyl-4,6-dioxo-1,3-dioxan-5-ylidene)-l3-iodaneyl)phenoxy)-3-phenylpropyl)(methyl)carbamate



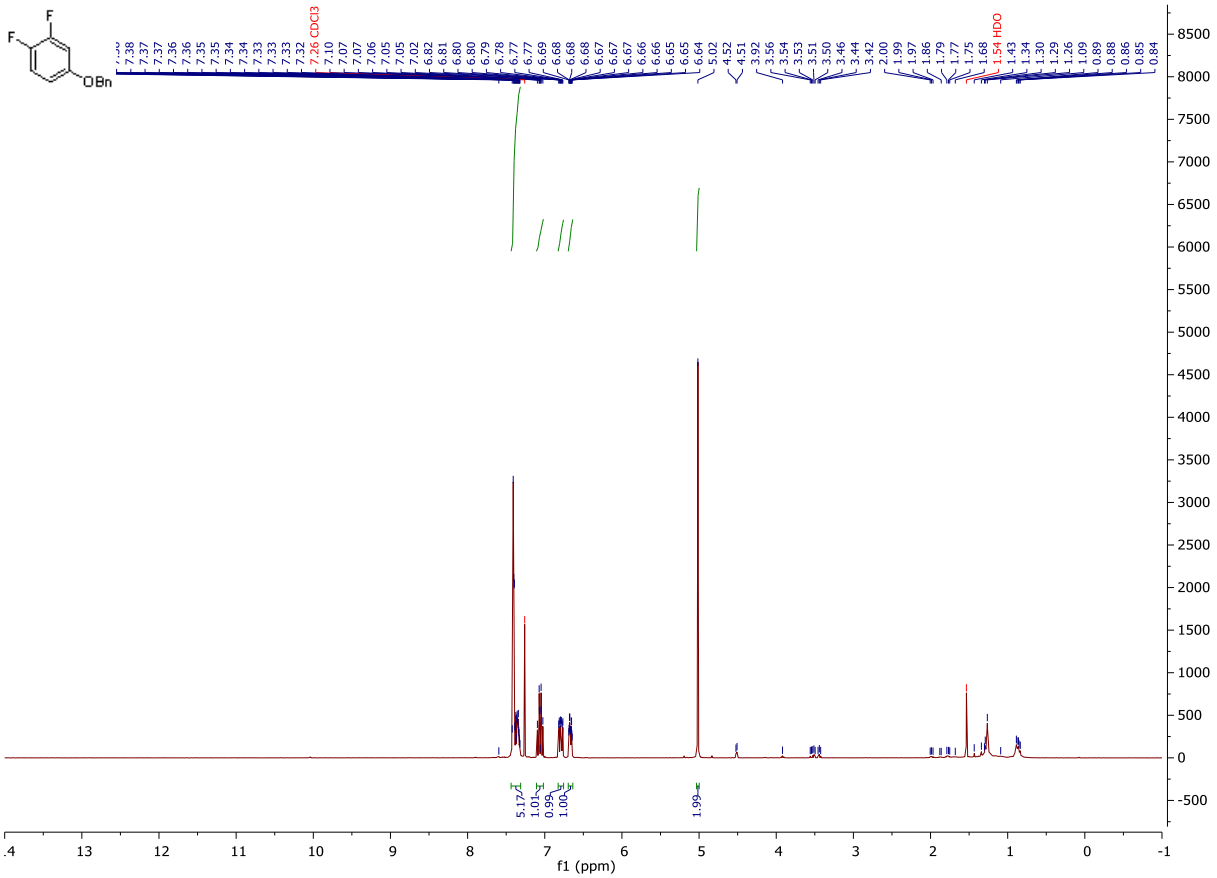
8-methyl-8-azabicyclo[3.2.1]octan-3-yl 4-((2,2-dimethyl-4,6-dioxo-1,3-dioxan-5-ylidene)-l3-iodaneyl)benzoate



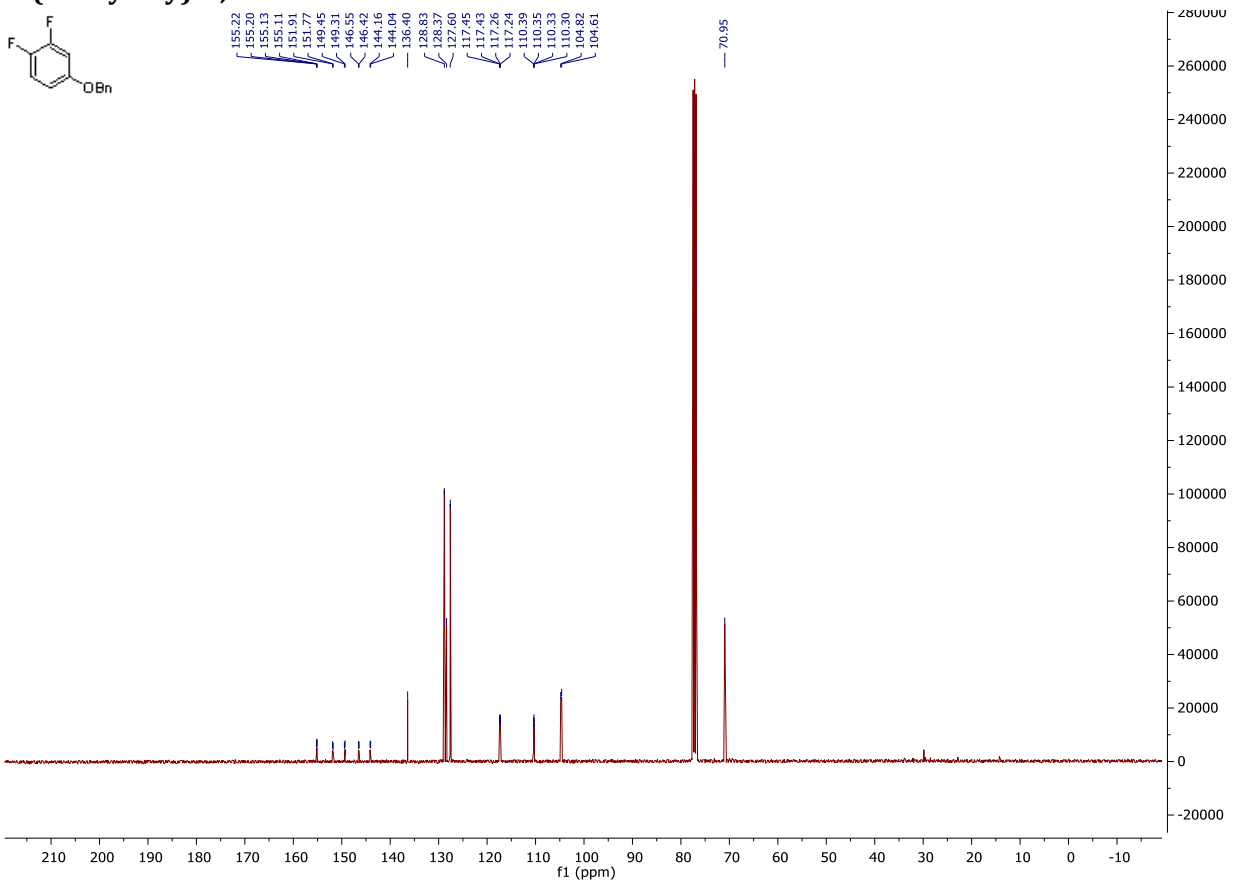
8-methyl-8-azabicyclo[3.2.1]octan-3-yl 4-((2,2-dimethyl-4,6-dioxo-1,3-dioxan-5-ylidene)-l3-iodaneyl)benzoate



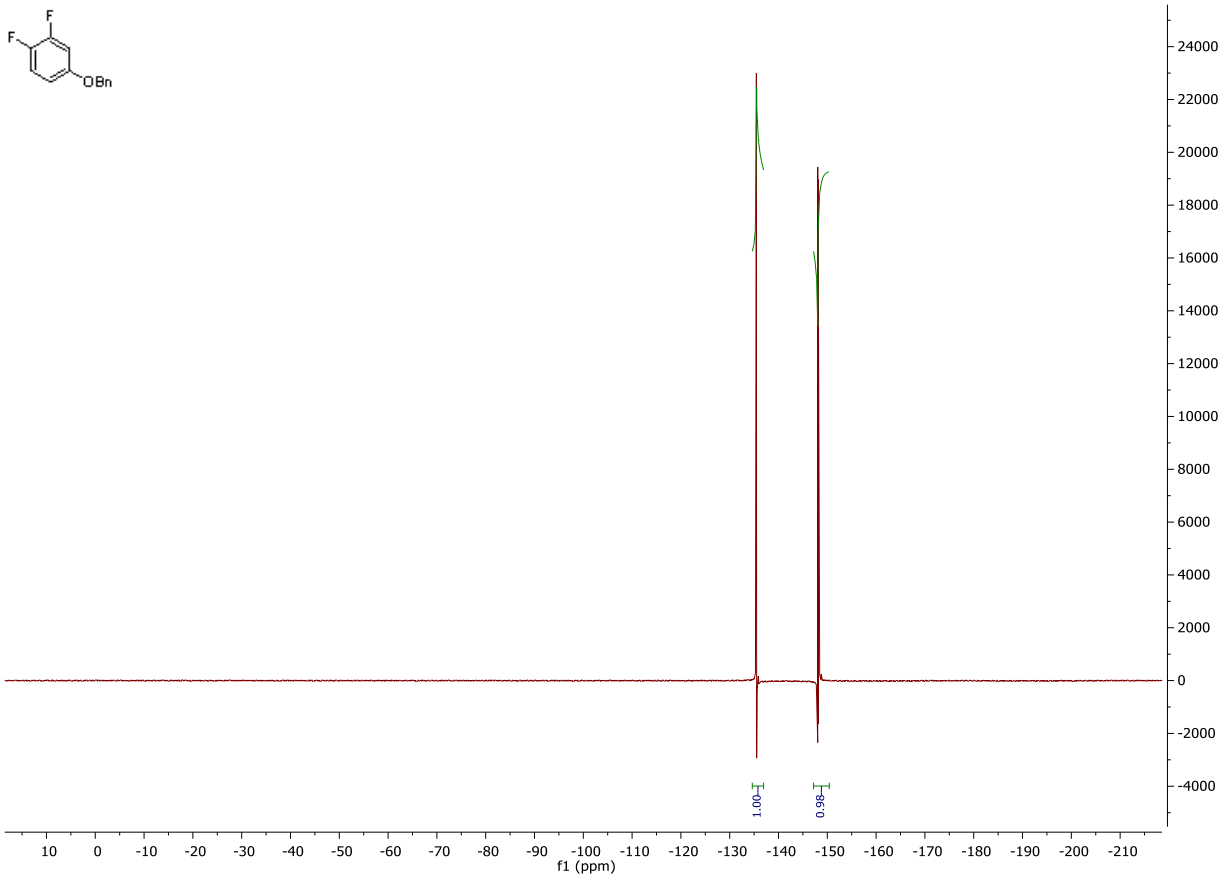
4-(benzyloxy)-1,2-difluorobenzene



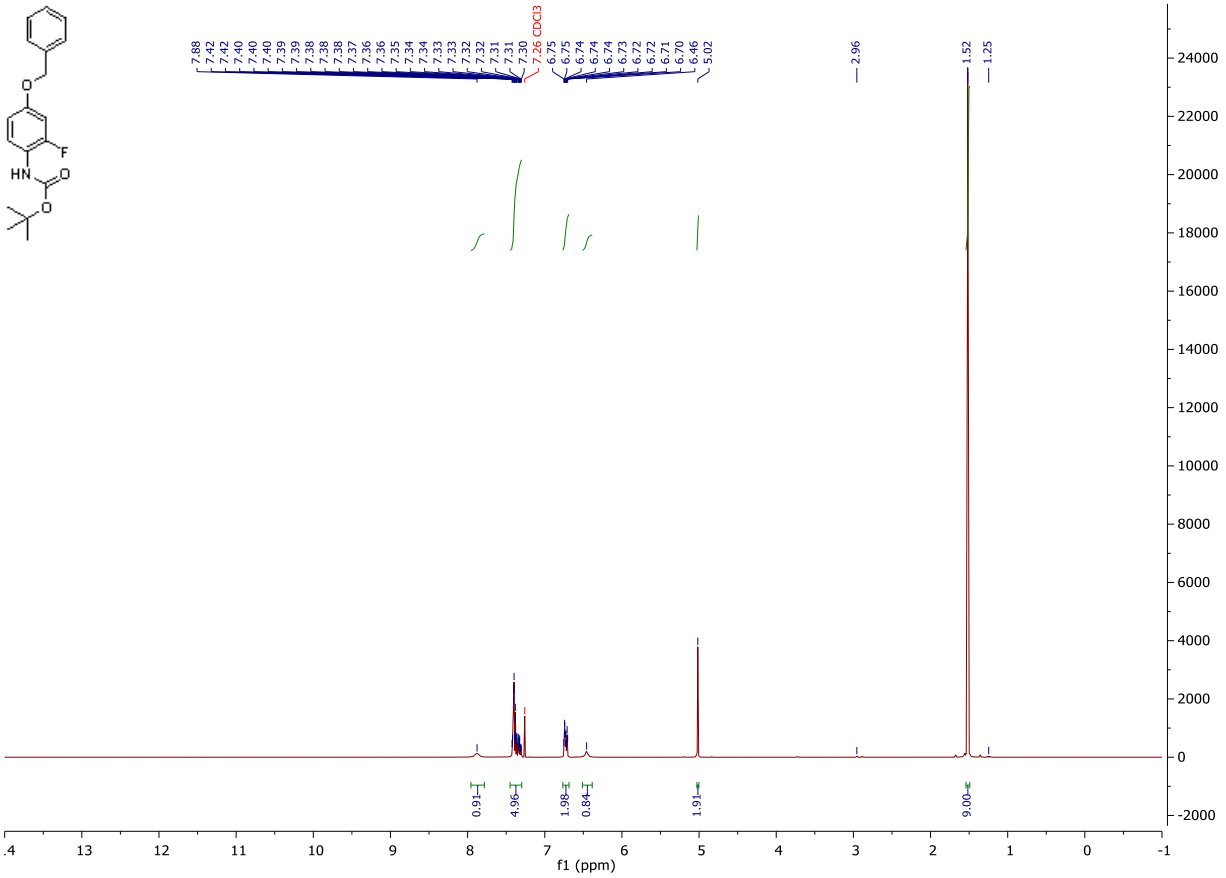
4-(benzyloxy)-1,2-difluorobenzene



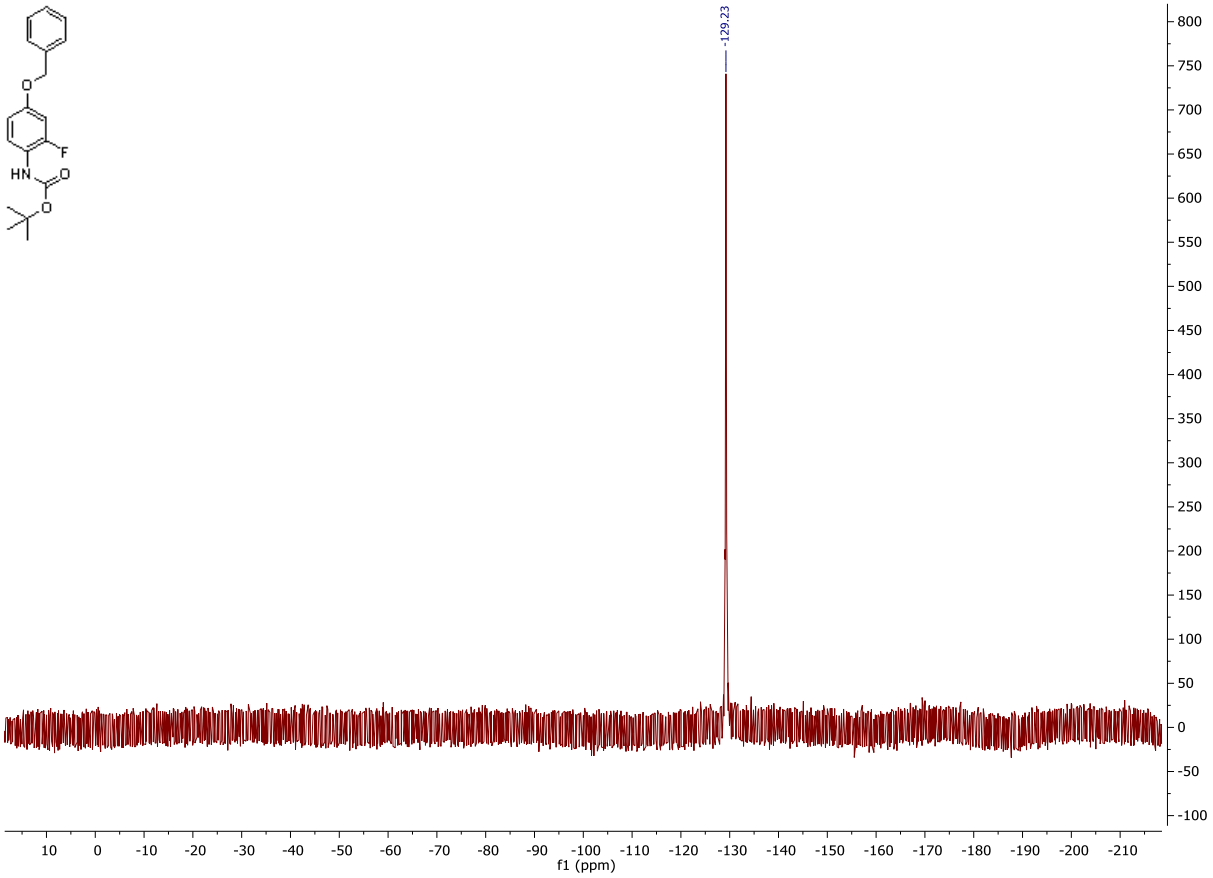
4-(benzyloxy)-1,2-difluorobenzene



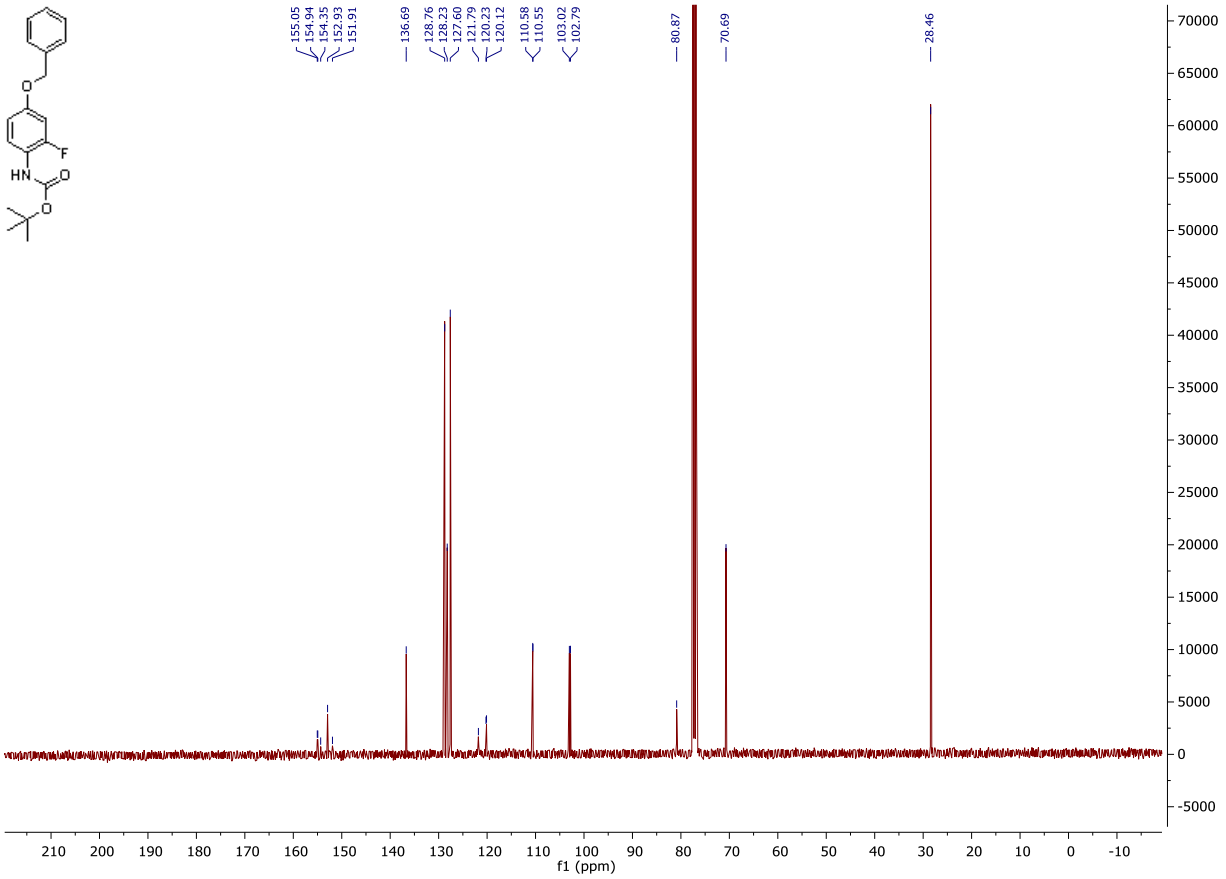
tert-butyl **(4-(benzyloxy)-2-fluorophenyl)carbamate**



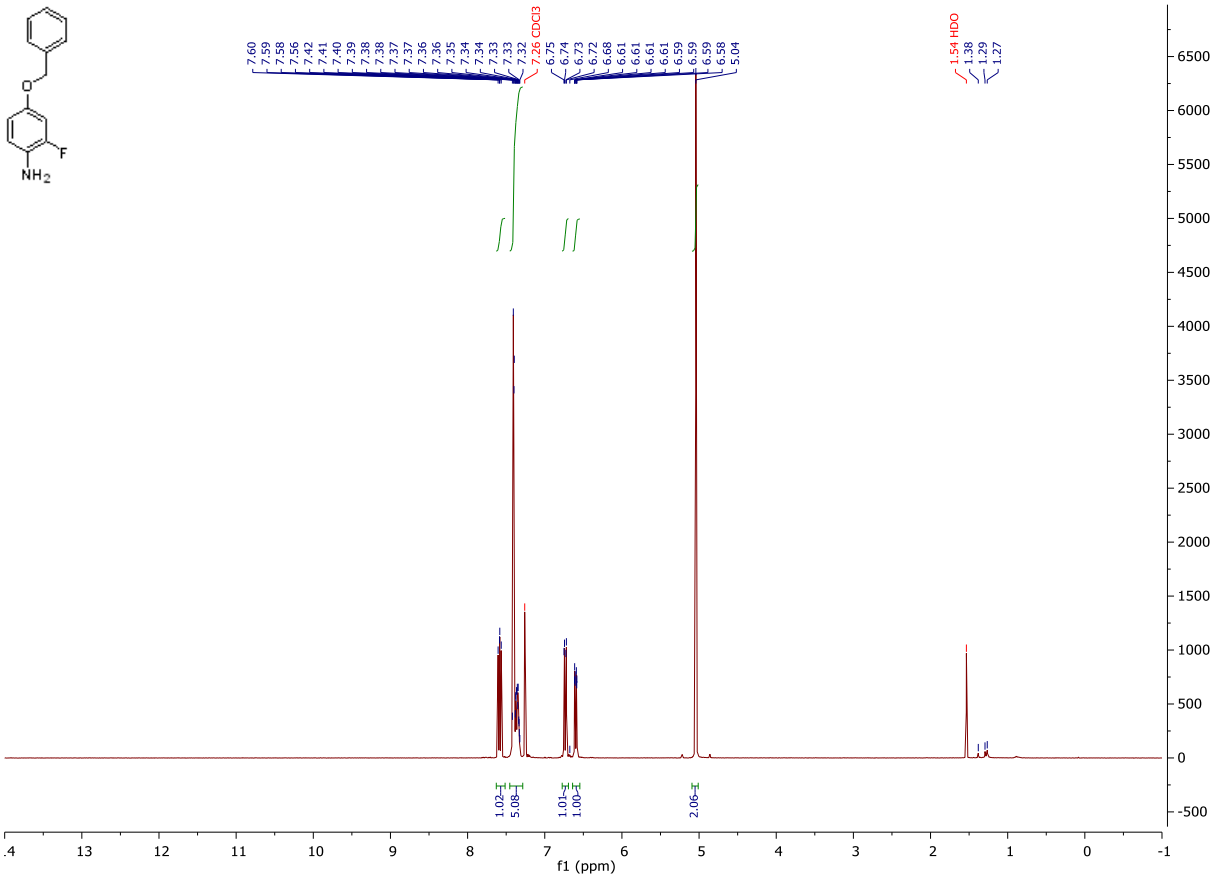
tert-butyl **(4-(benzyloxy)-2-fluorophenyl)carbamate**



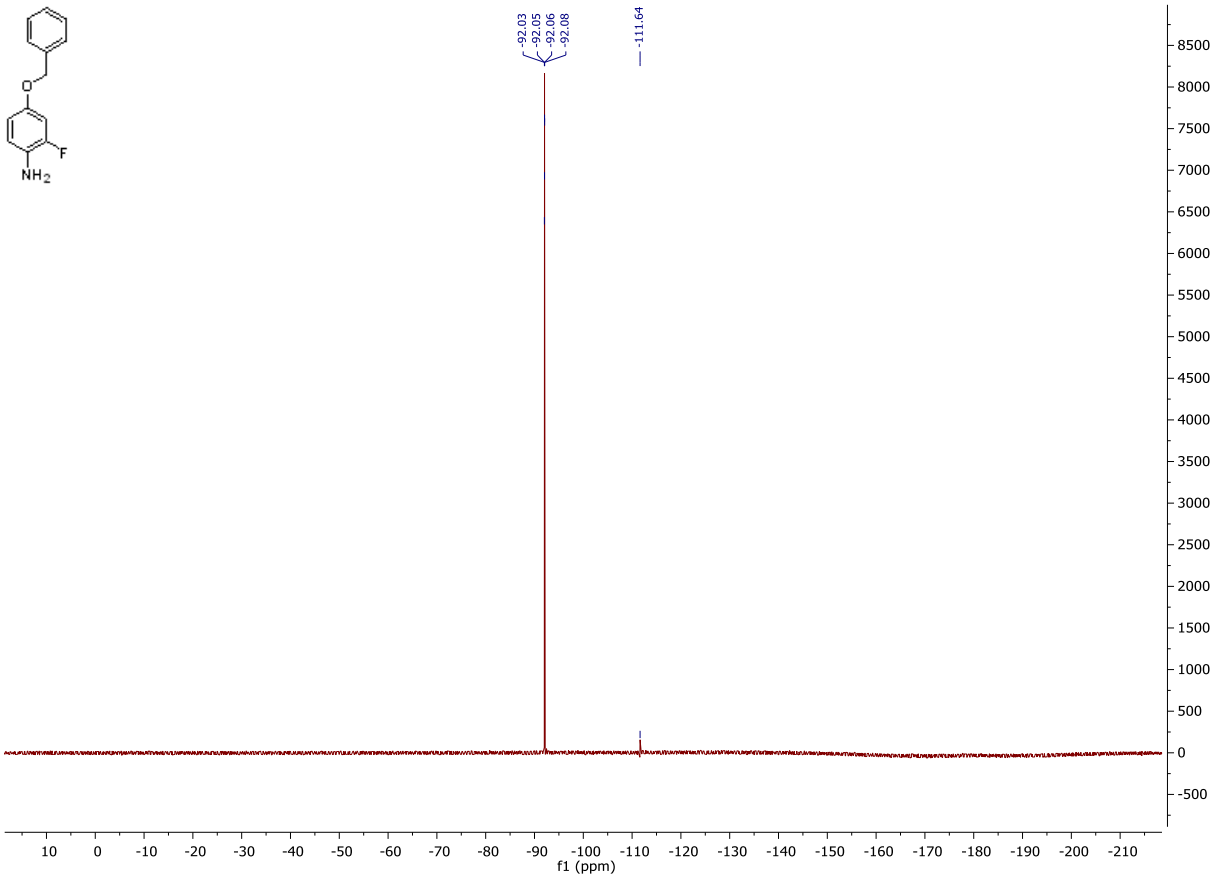
tert-butyl (4-(benzyloxy)-2-fluorophenyl)carbamate



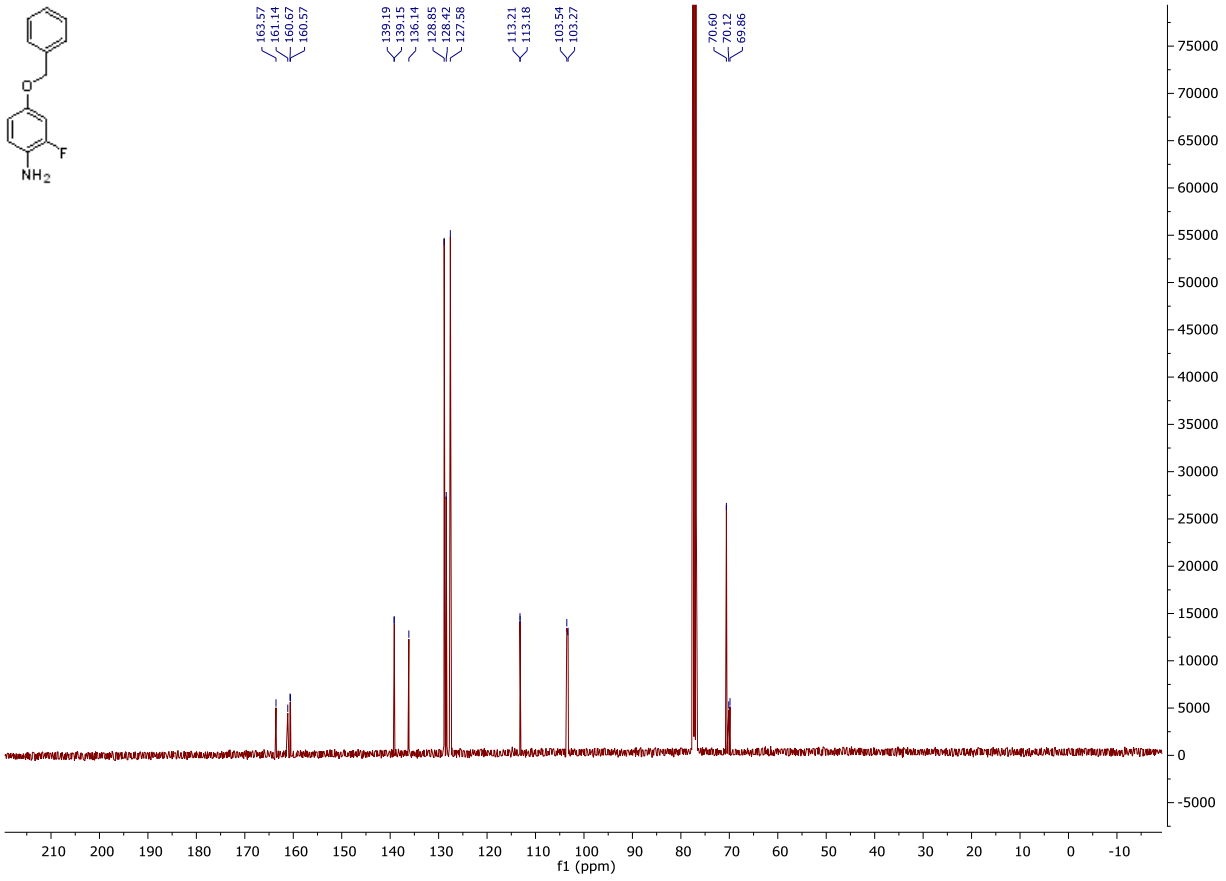
4-(benzyloxy)-2-fluoroaniline



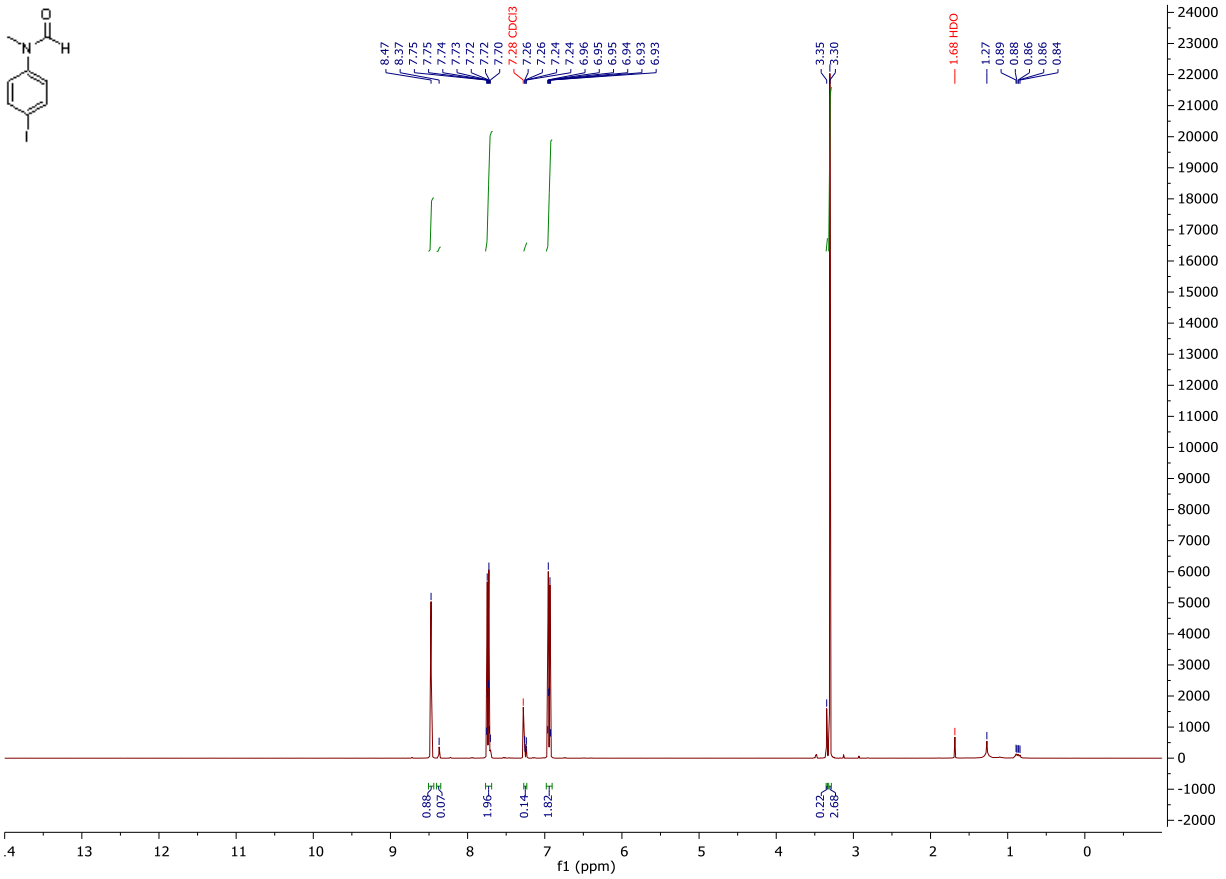
4-(benzyloxy)-2-fluoroaniline

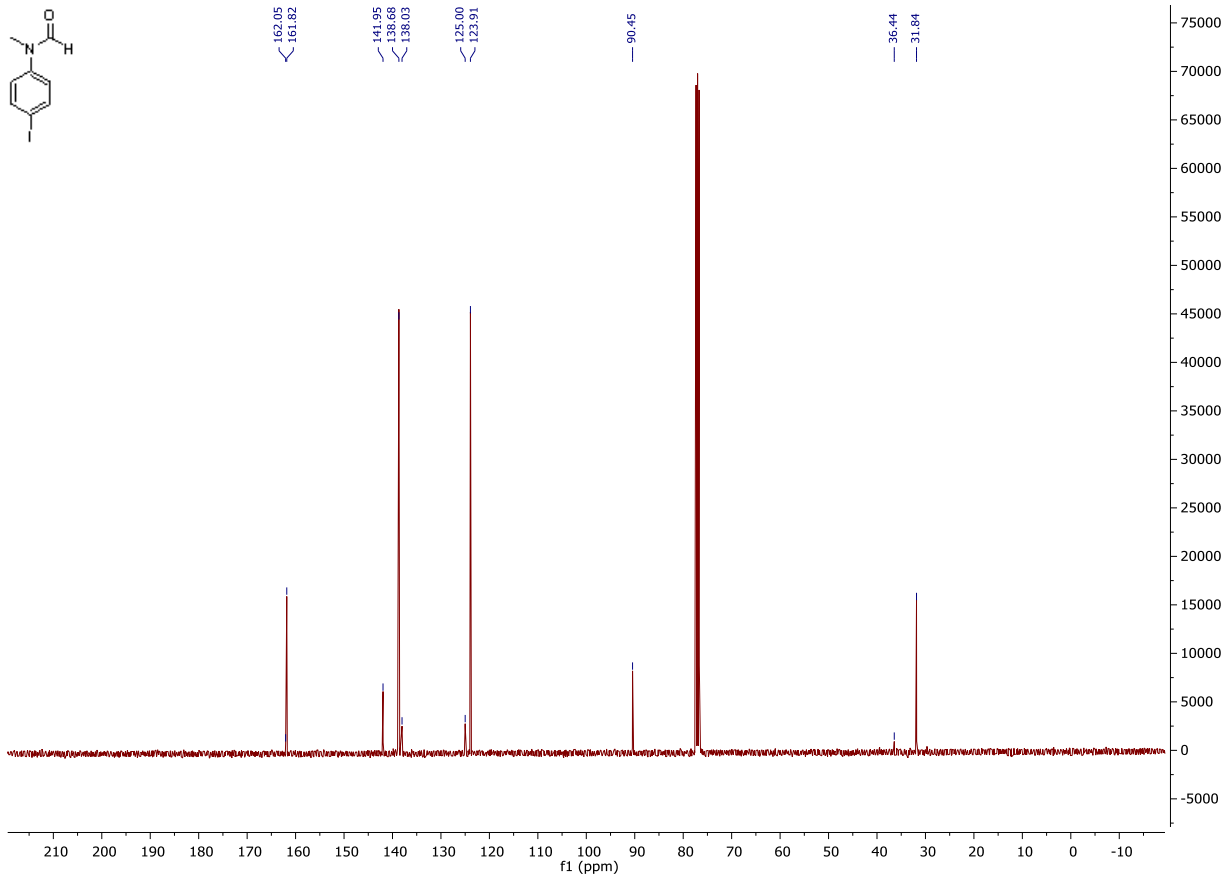


4-(benzyloxy)-2-fluoroaniline

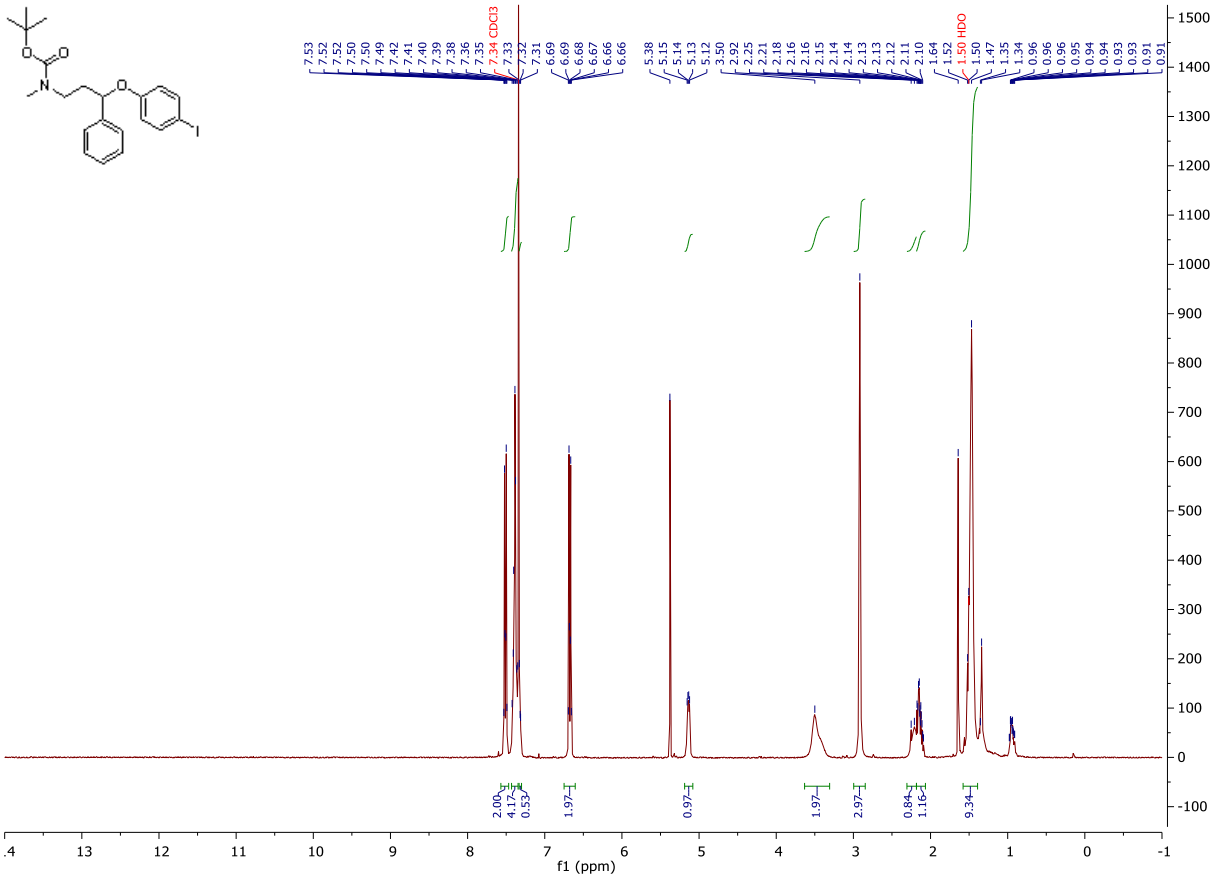


N-(4-iodophenyl)-N-methylformamide

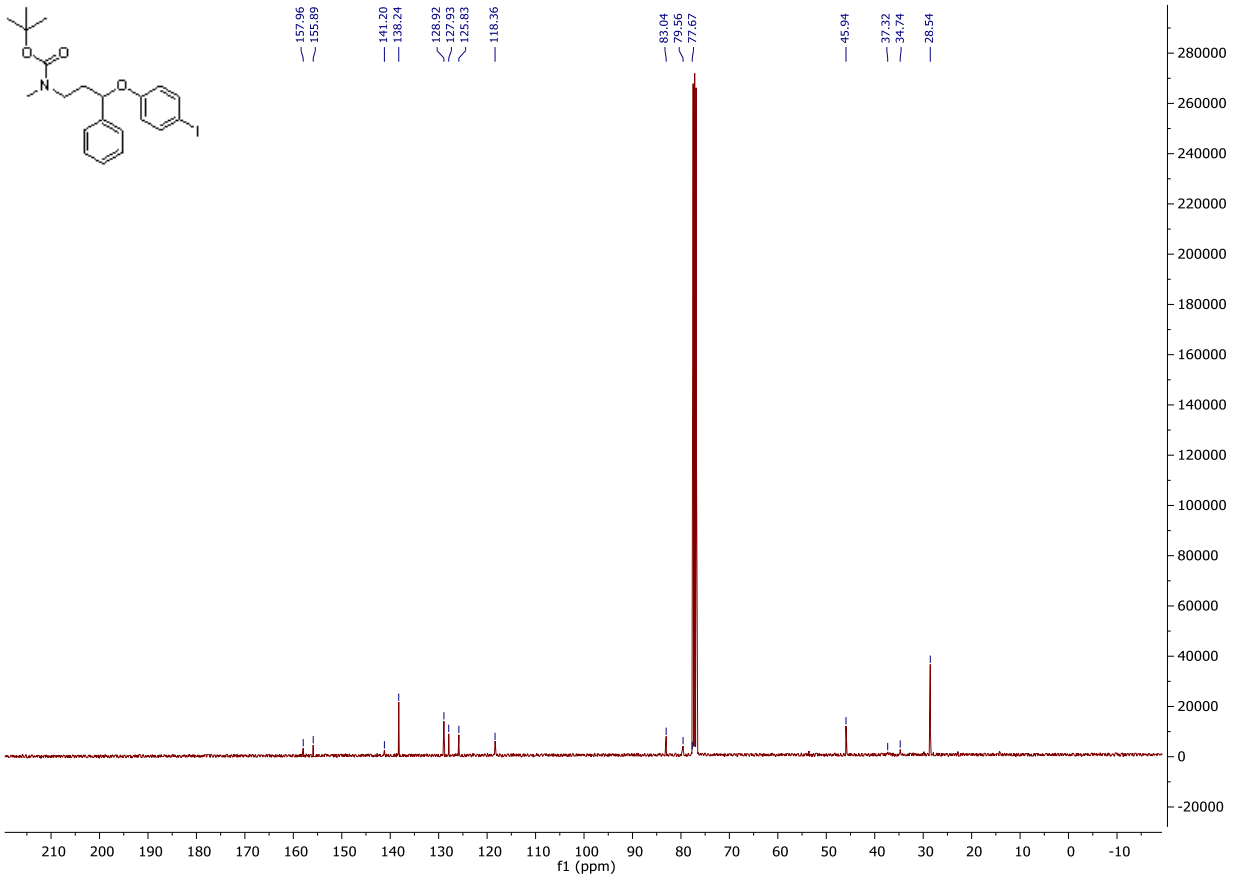



162.05
161.82
141.95
138.68
138.03
125.00
123.91
90.45
36.44
31.84
75000
70000
65000
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

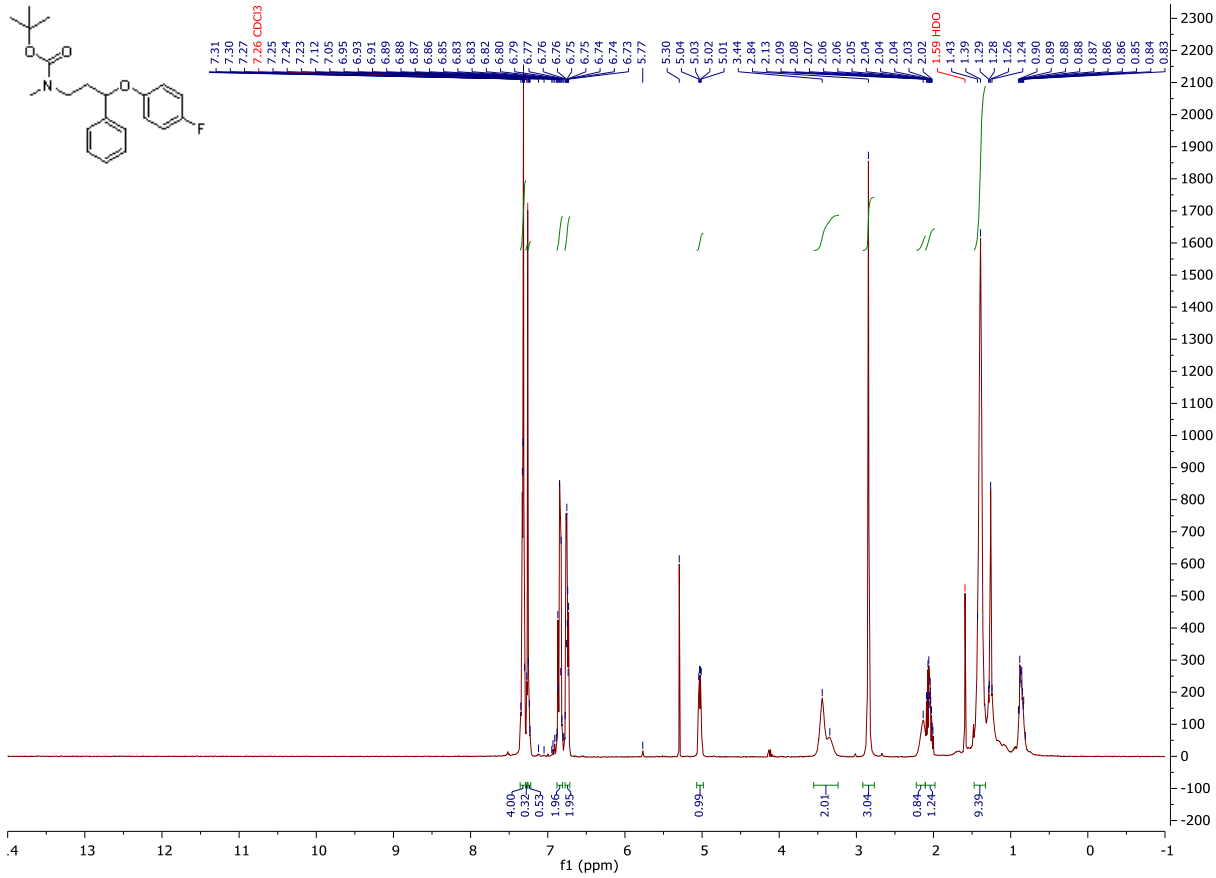
tert-butyl (3-(4-iodophenoxy)-3-phenylpropyl)(methyl)carbamate



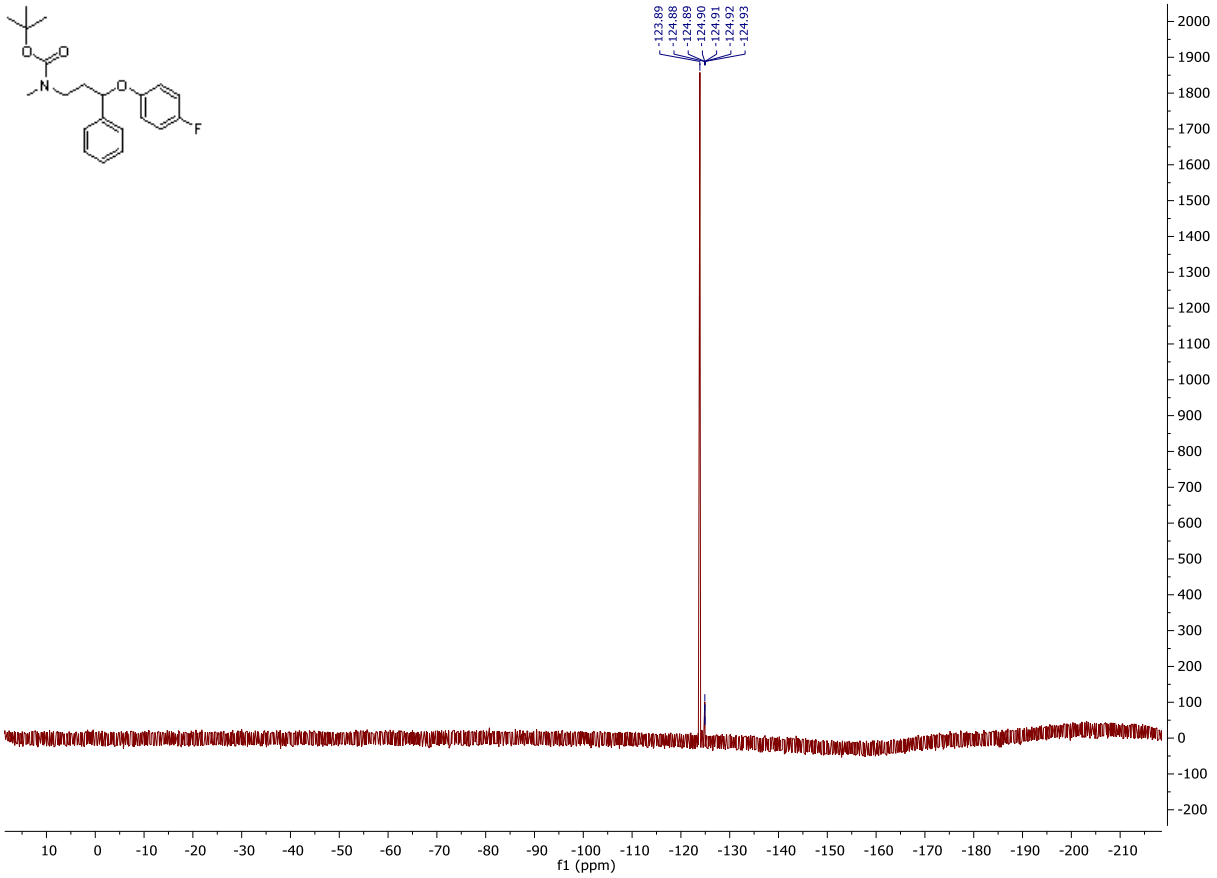
tert-butyl (3-(4-iodophenoxy)-3-phenylpropyl)(methyl)carbamate



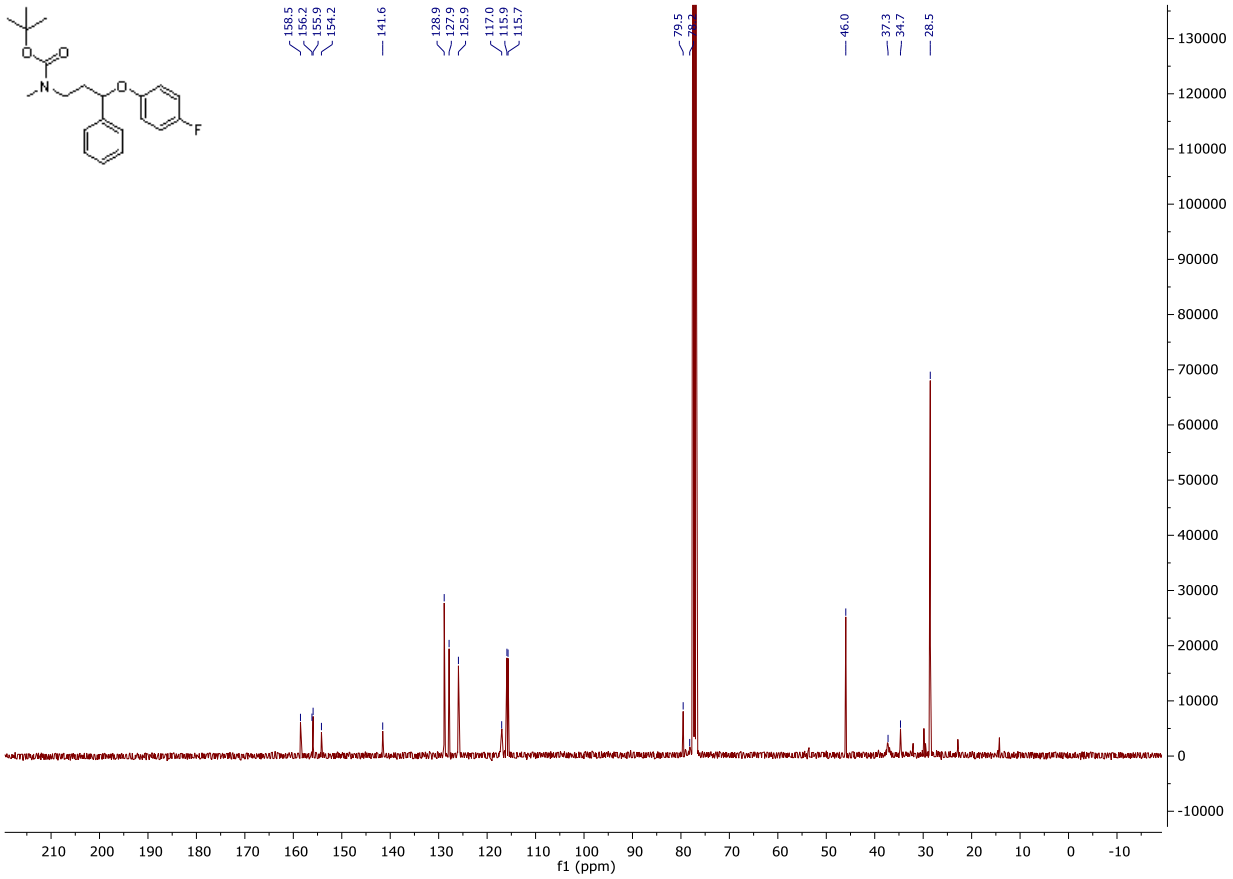
tert-butyl (3-(4-fluorophenoxy)-3-phenylpropyl)(methyl)carbamate



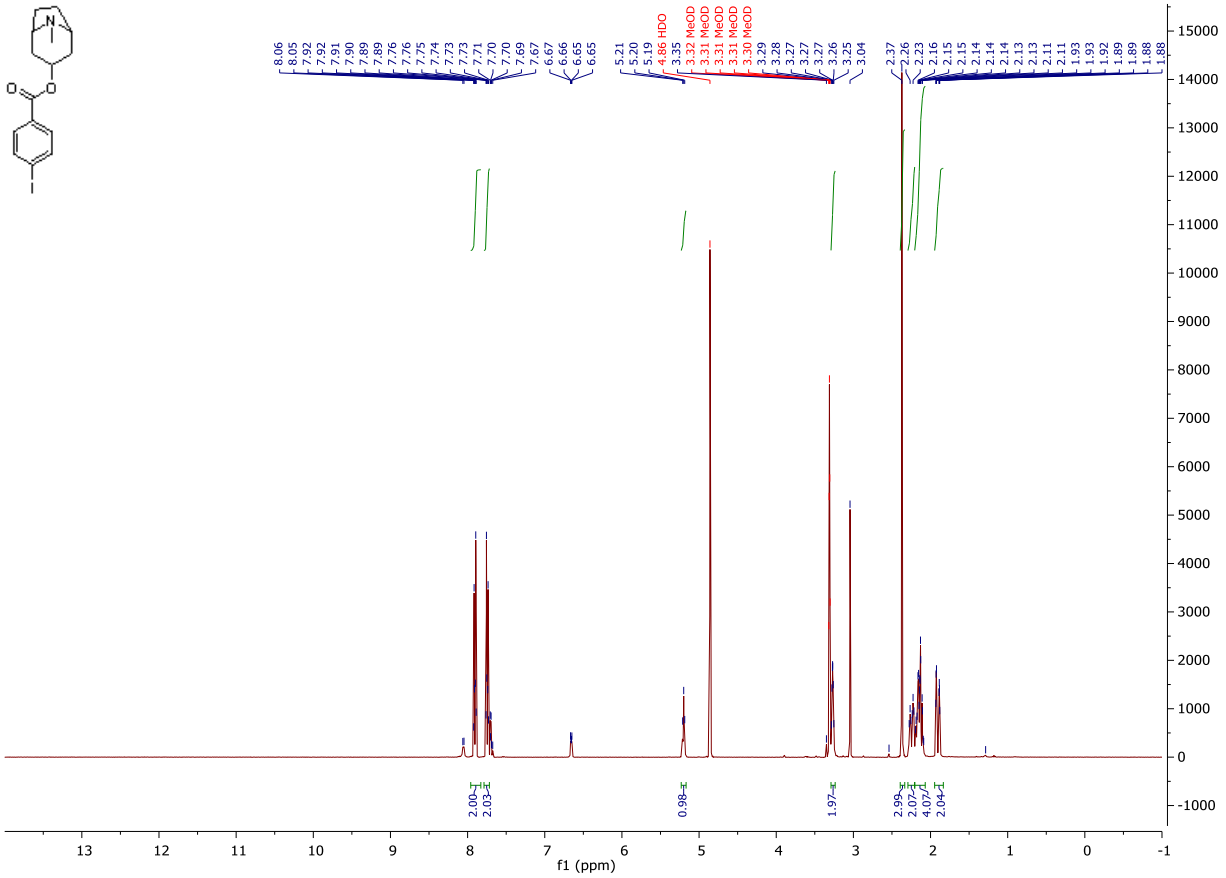
tert-butyl (3-(4-fluorophenoxy)-3-phenylpropyl)(methyl)carbamate



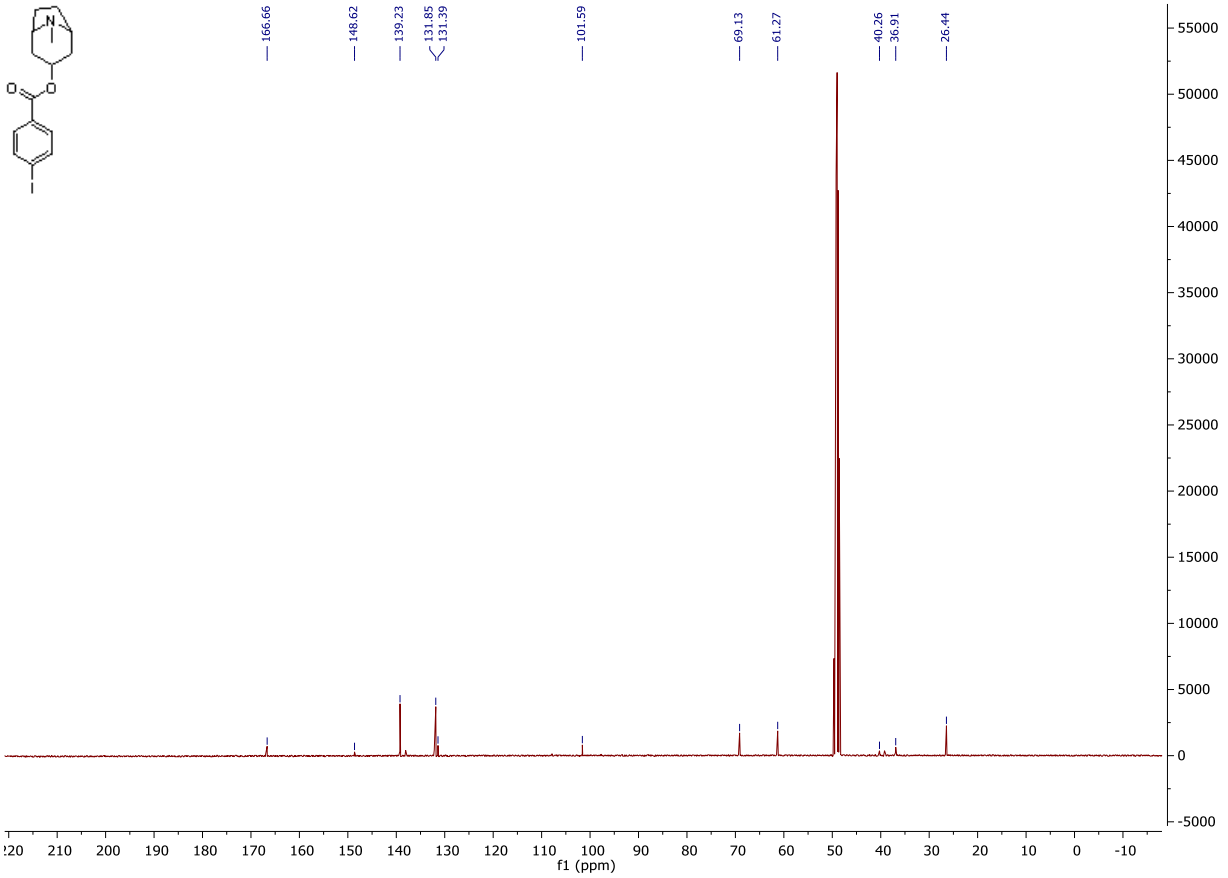
tert-butyl (3-(4-fluorophenoxy)-3-phenylpropyl)(methyl)carbamate



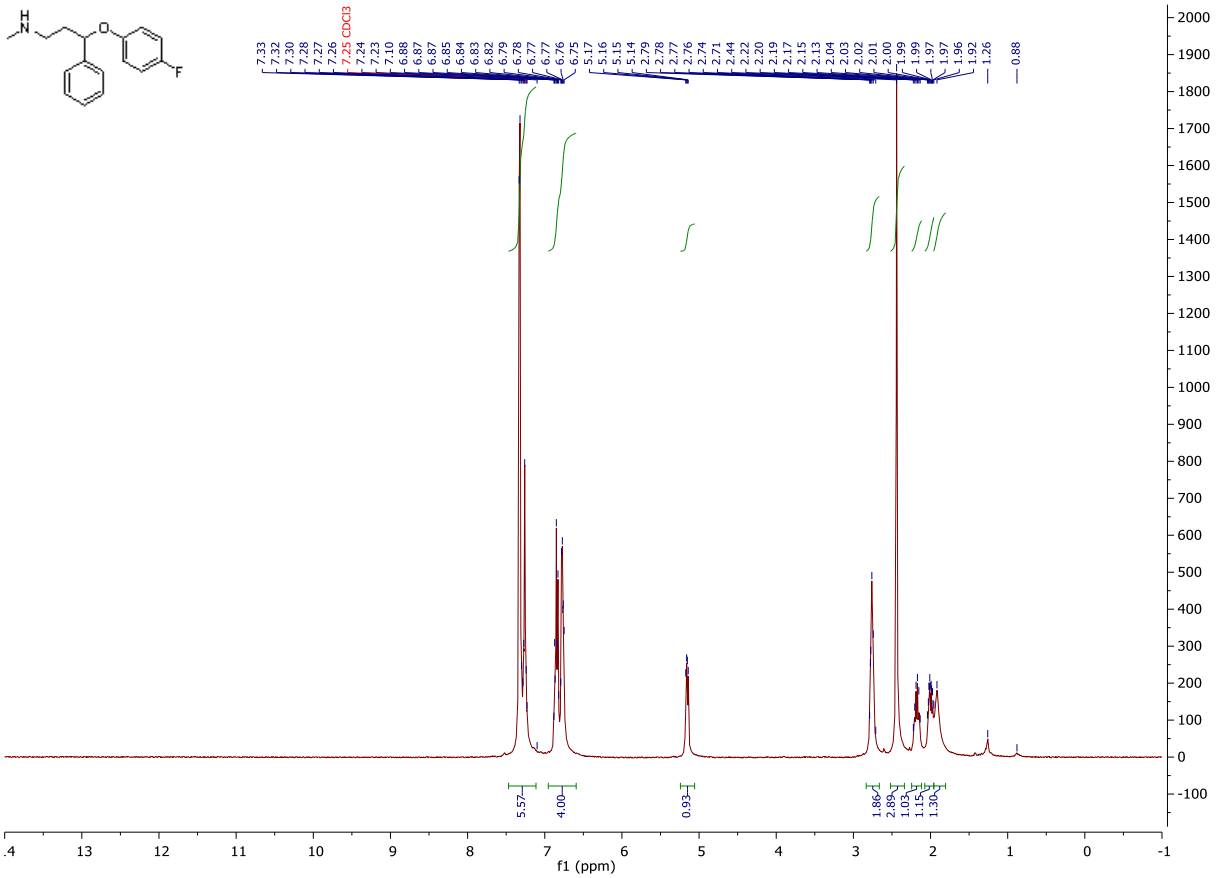
8-methyl-8-azabicyclo[3.2.1]octan-3-yl **4-iodobenzoate**



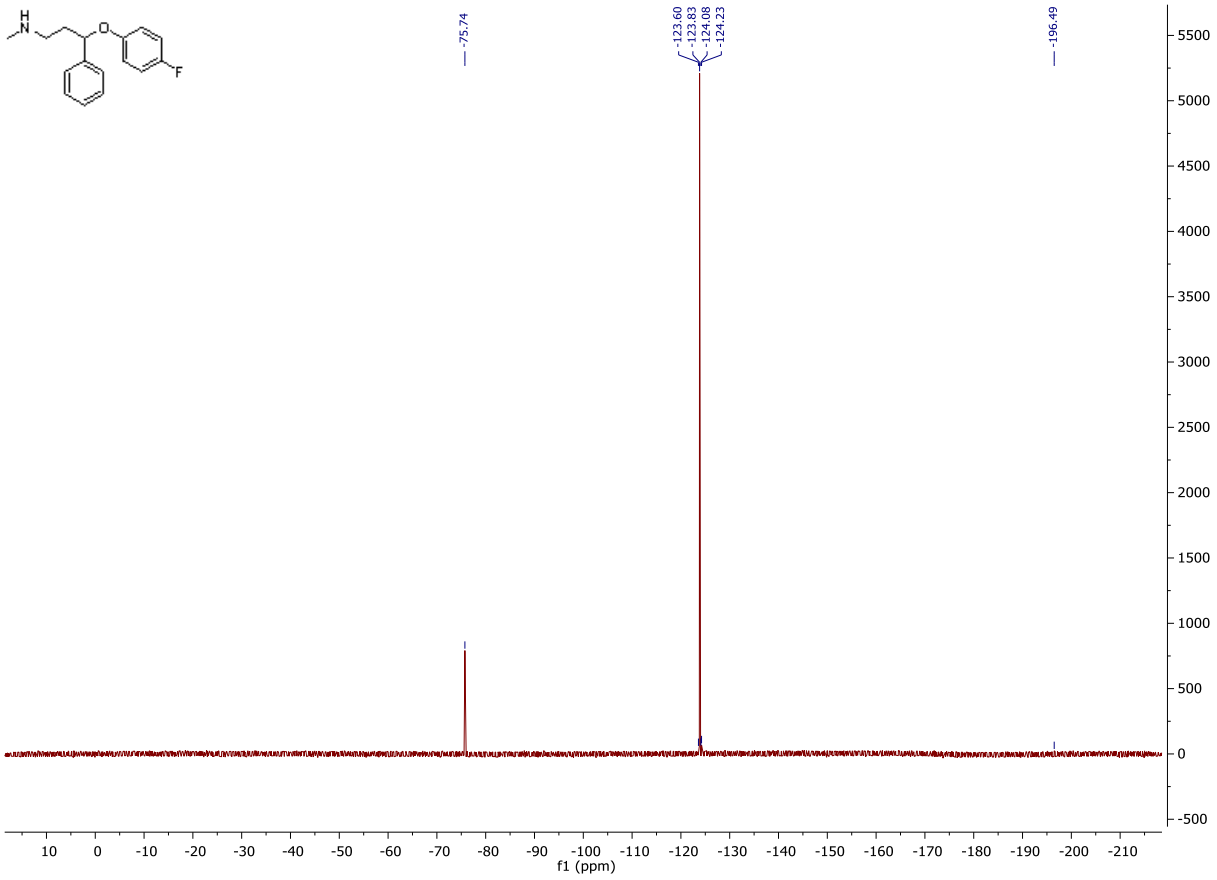
8-methyl-8-azabicyclo[3.2.1]octan-3-yl **4-iodobenzoate**



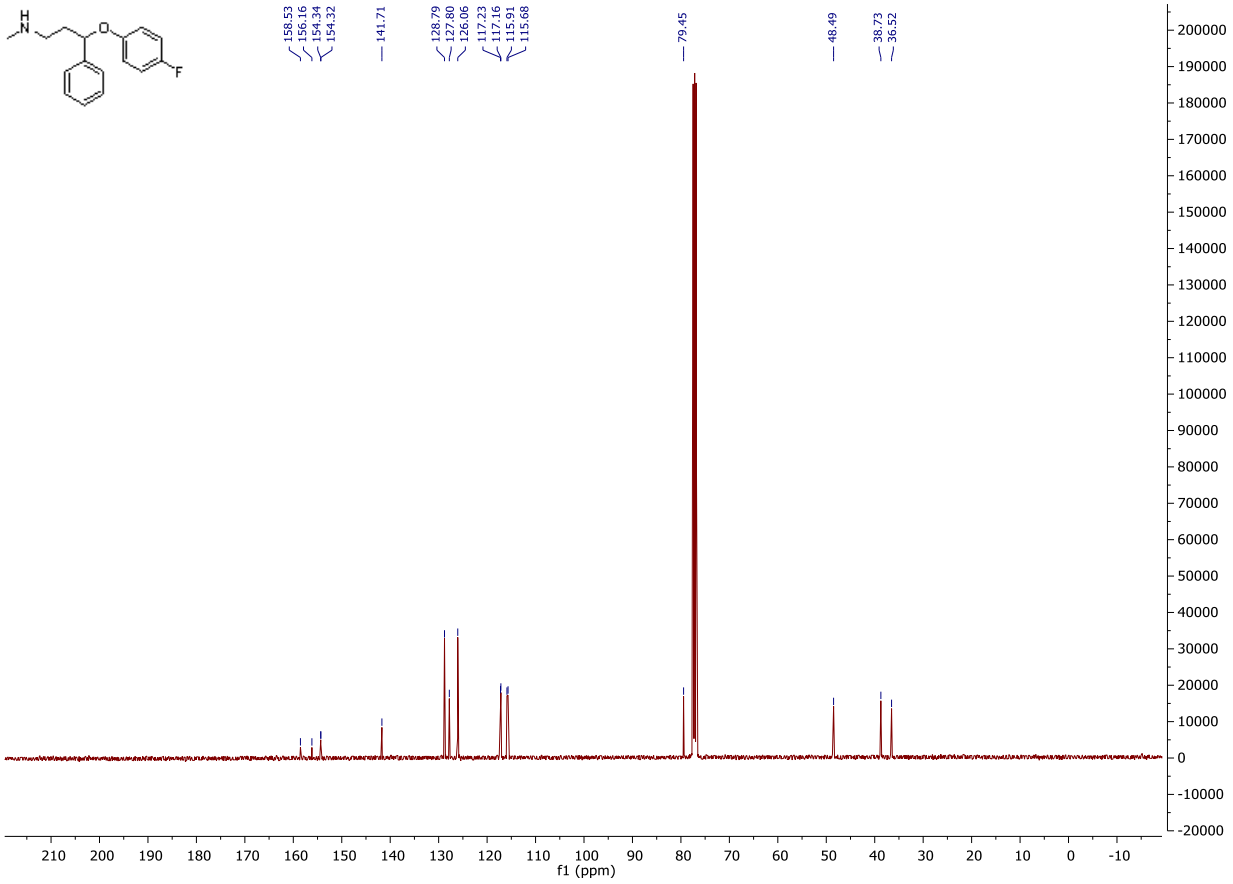
3-(4-fluorophenoxy)-N-methyl-3-phenylpropan-1-amine



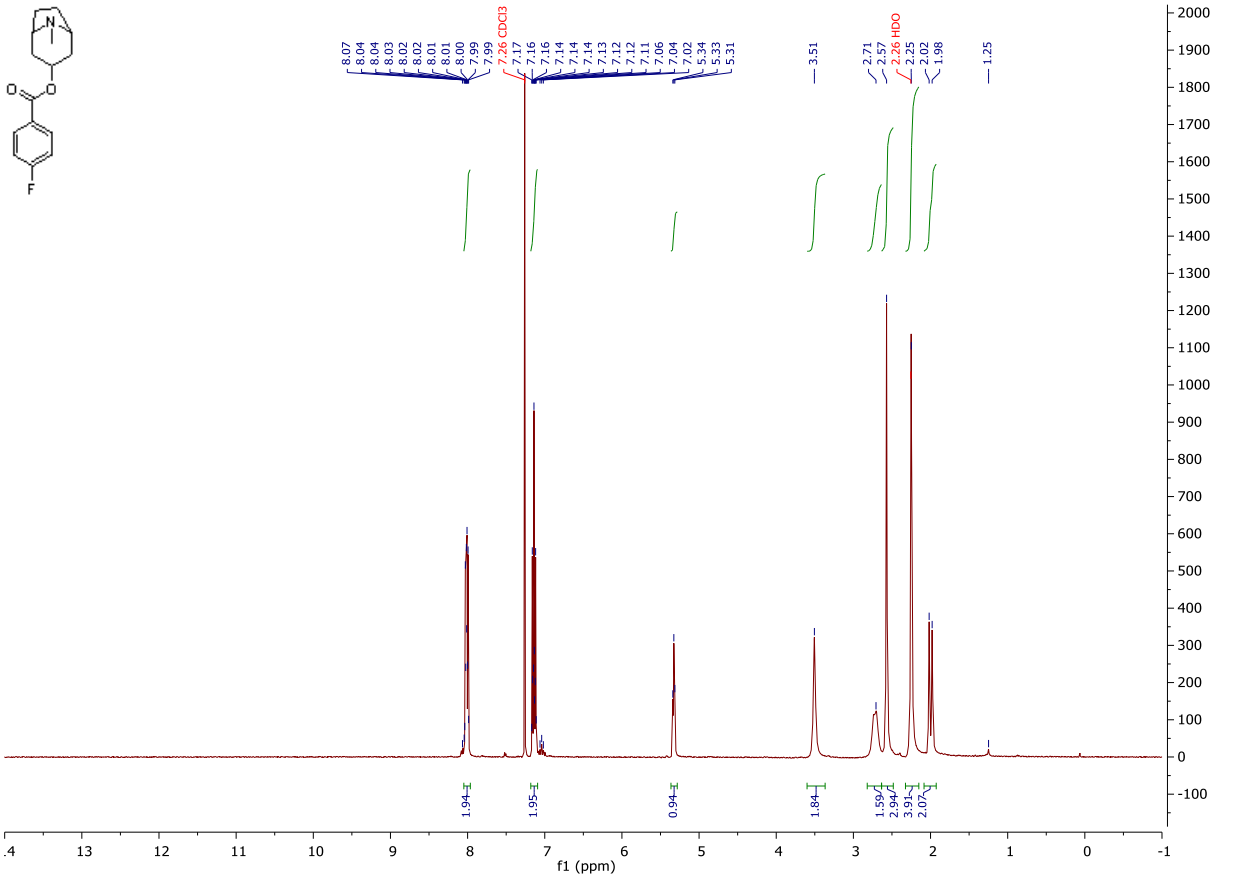
3-(4-fluorophenoxy)-N-methyl-3-phenylpropan-1-amine



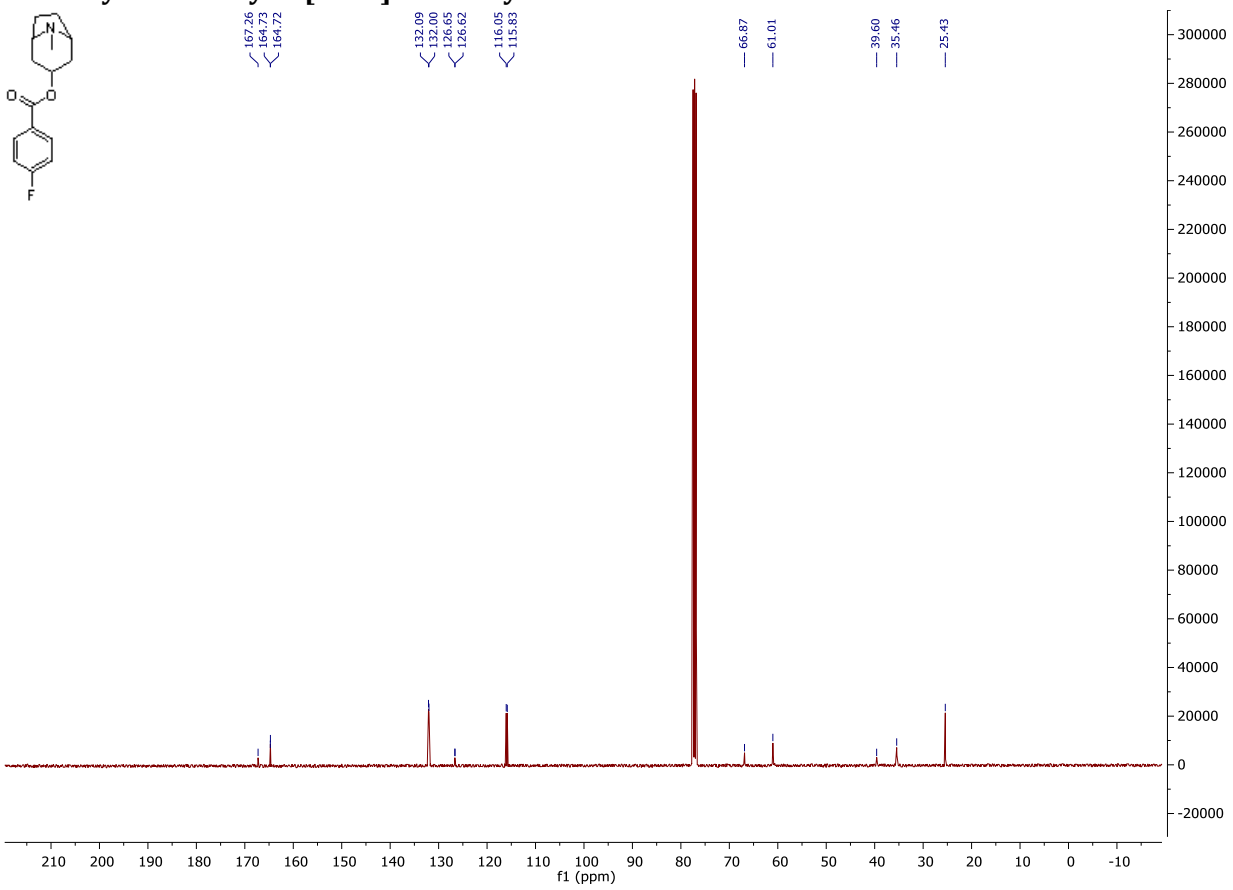
3-(4-fluorophenoxy)-N-methyl-3-phenylpropan-1-amine



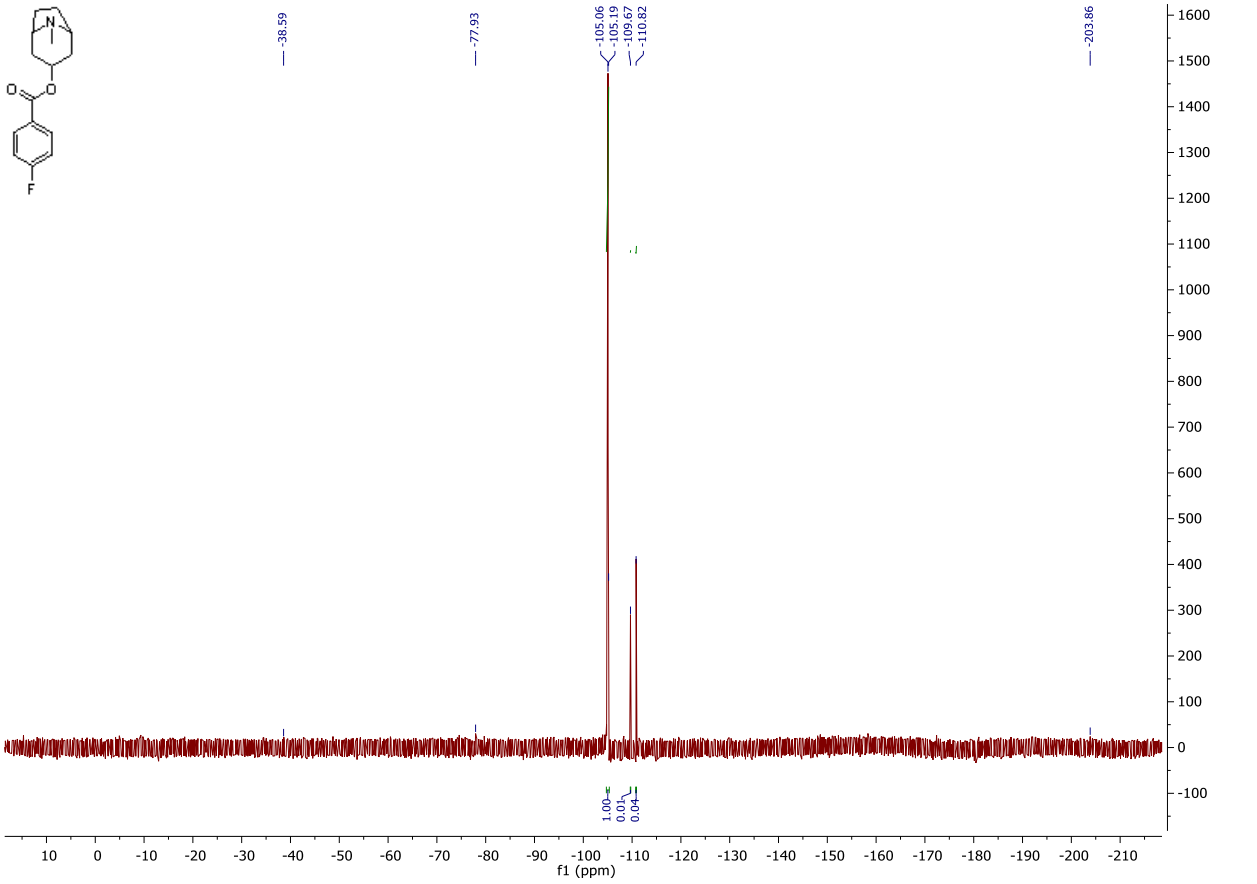
8-methyl-8-azabicyclo[3.2.1]octan-3-yl **4-fluorobenzoate**



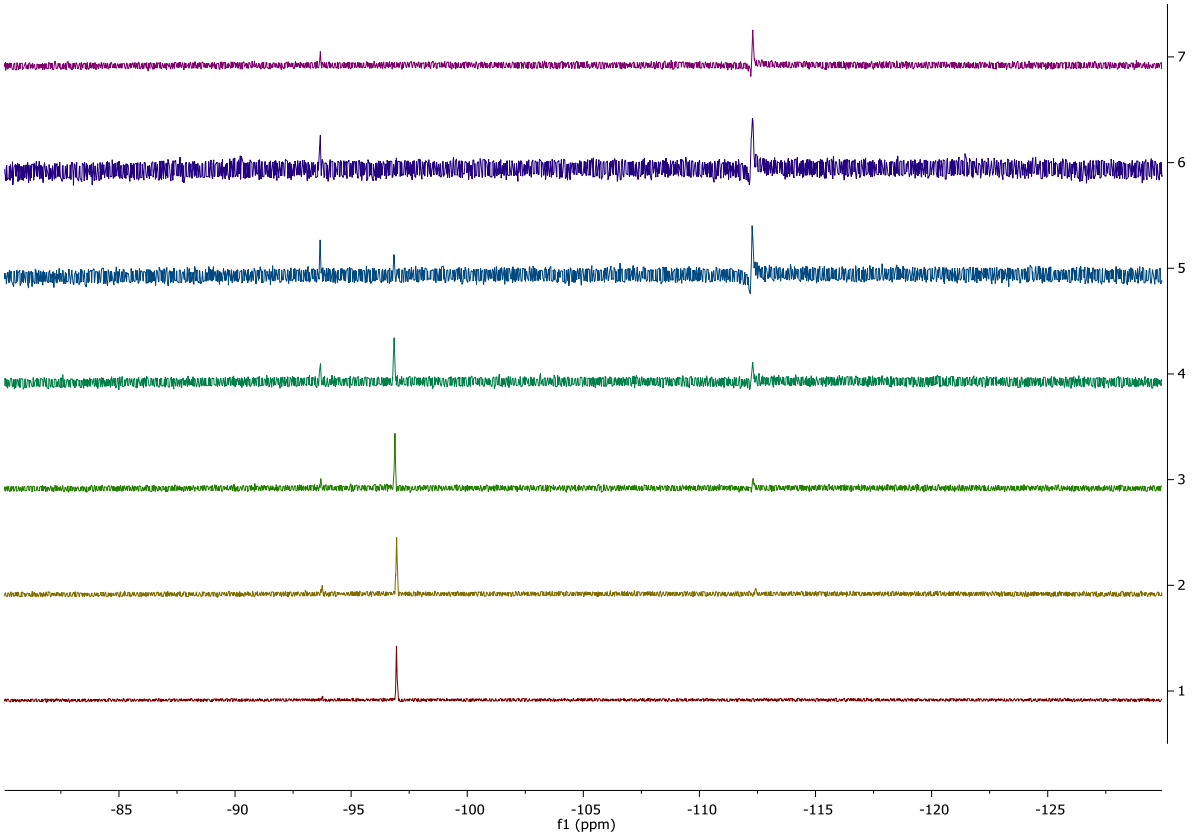
8-methyl-8-azabicyclo[3.2.1]octan-3-yl **4-fluorobenzoate**



8-methyl-8-azabicyclo[3.2.1]octan-3-yl **4-fluorobenzoate**

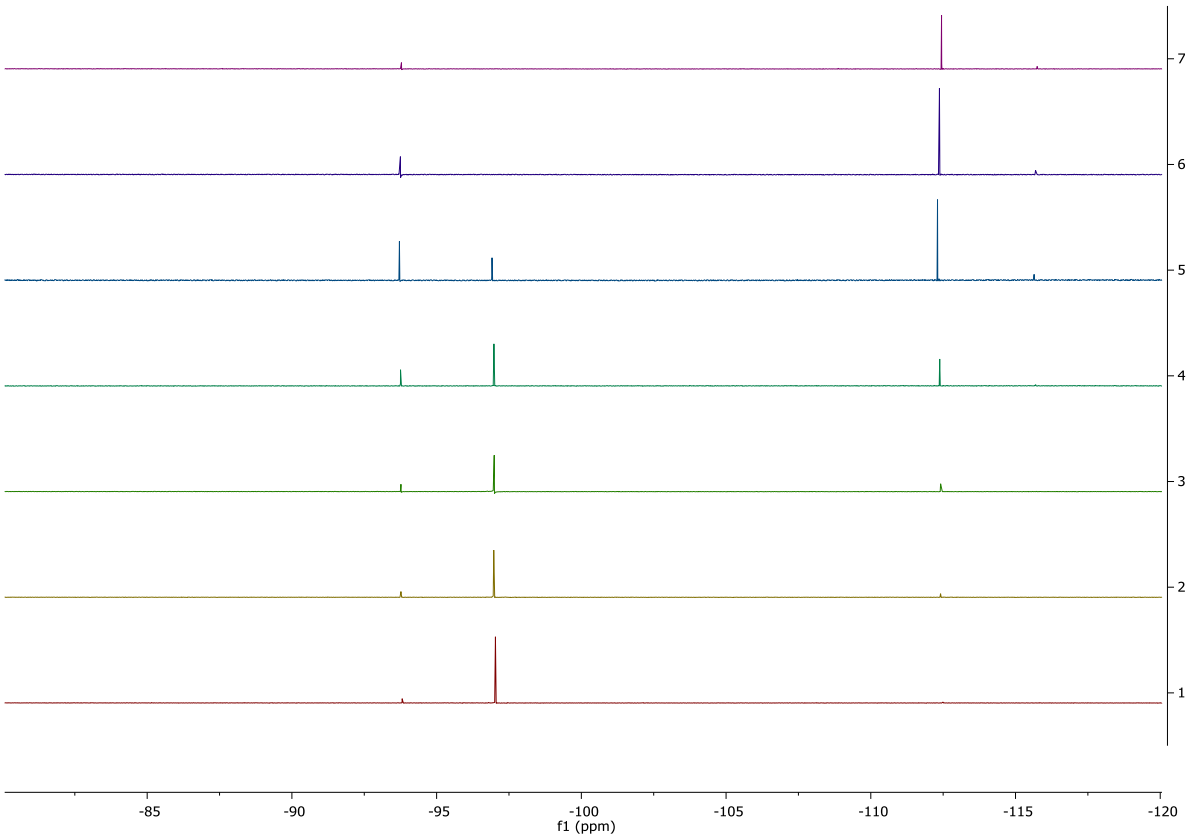


NMR degradation standard conditions



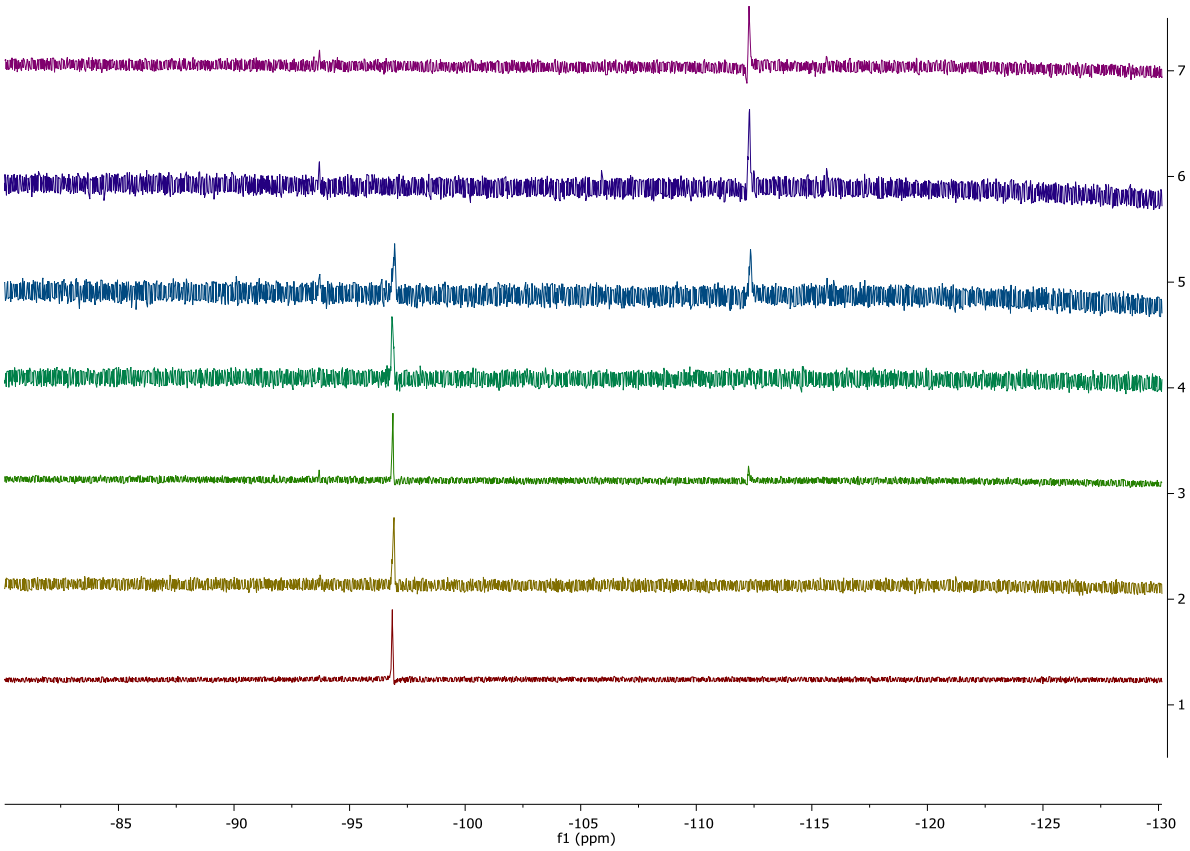
After 0, 2, 3, 4, 6, 10, 20 minutes starting from bottom.

NMR degradation standard conditions



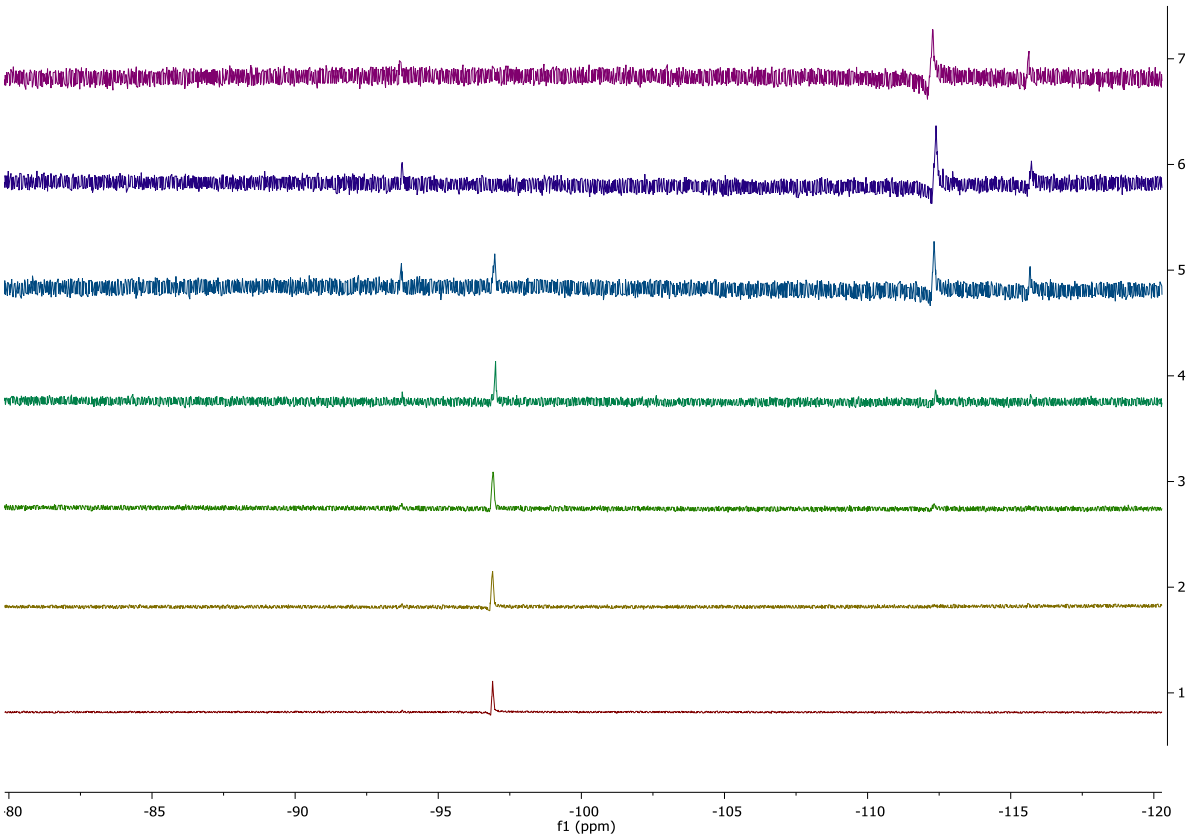
After 0, 2, 3, 4, 6, 10, 20 minutes starting from bottom.

NMR degradation standard conditions + 100mol% PPh_3



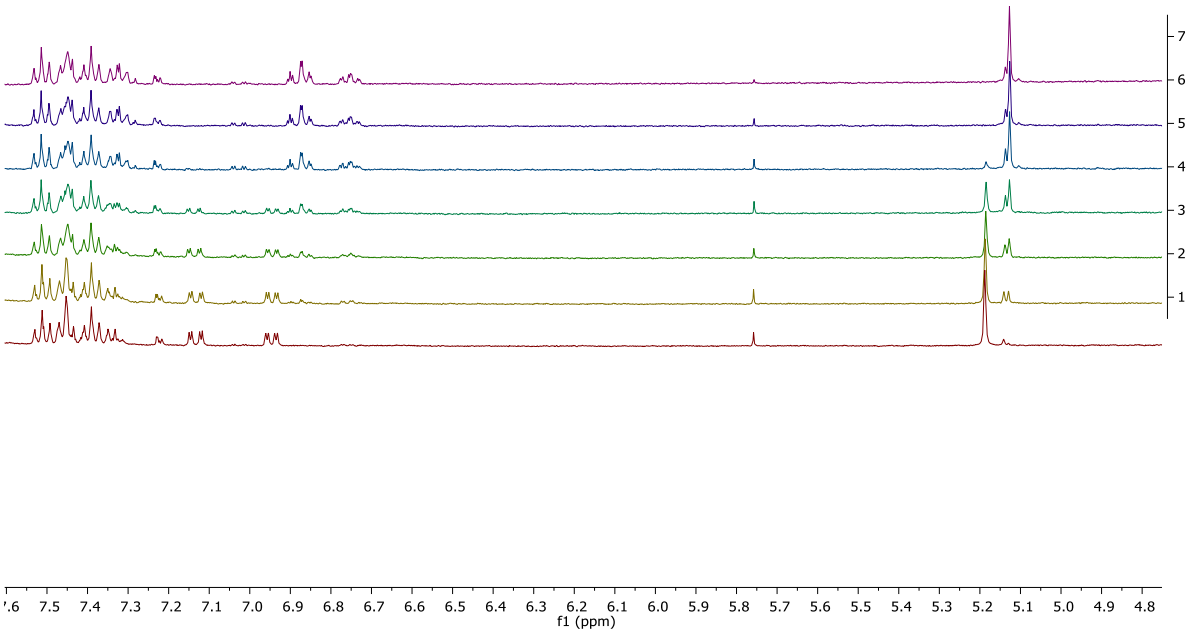
After 0, 2, 3, 4, 6, 10, 20 minutes starting from bottom.

NMR degradation standard conditions + 100mol% PPh_3



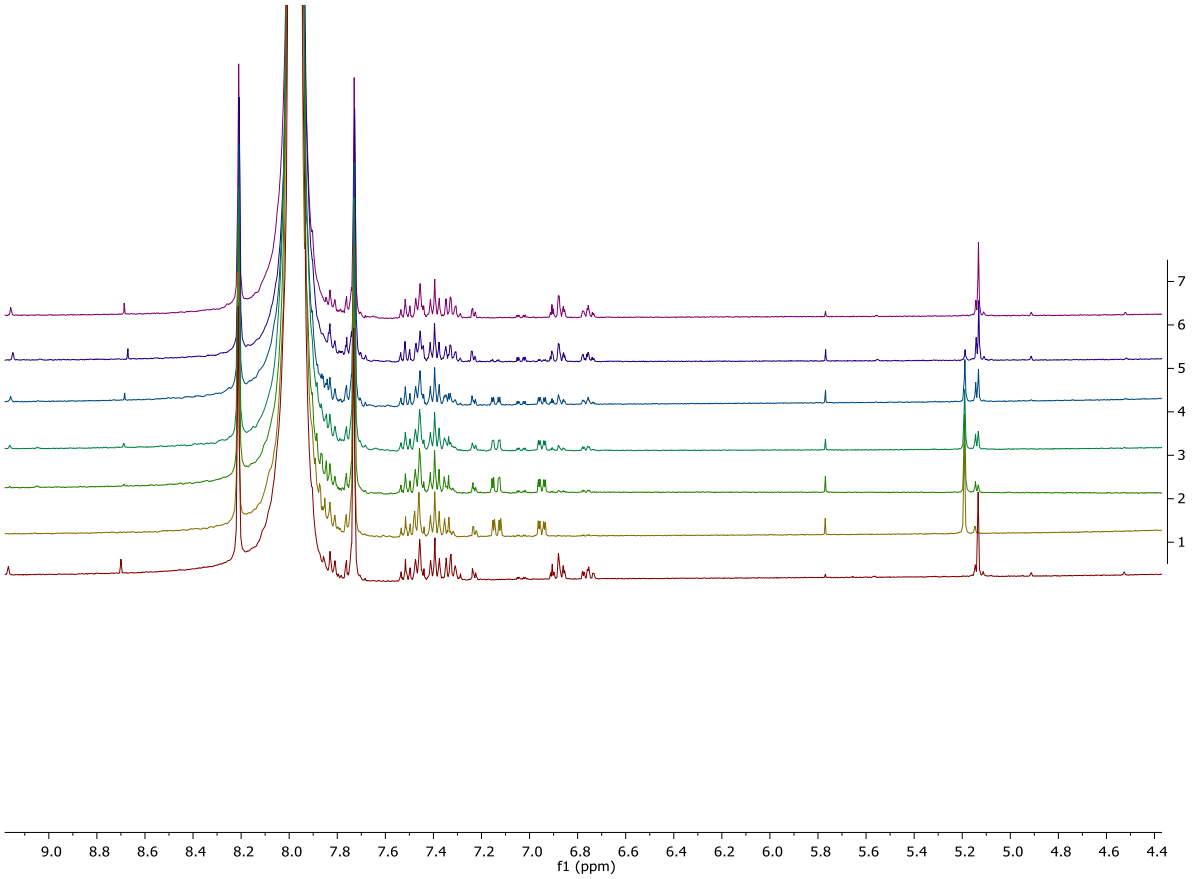
After 0, 2, 3, 4, 6, 10, 20 minutes starting from bottom.

NMR degradation standard conditions



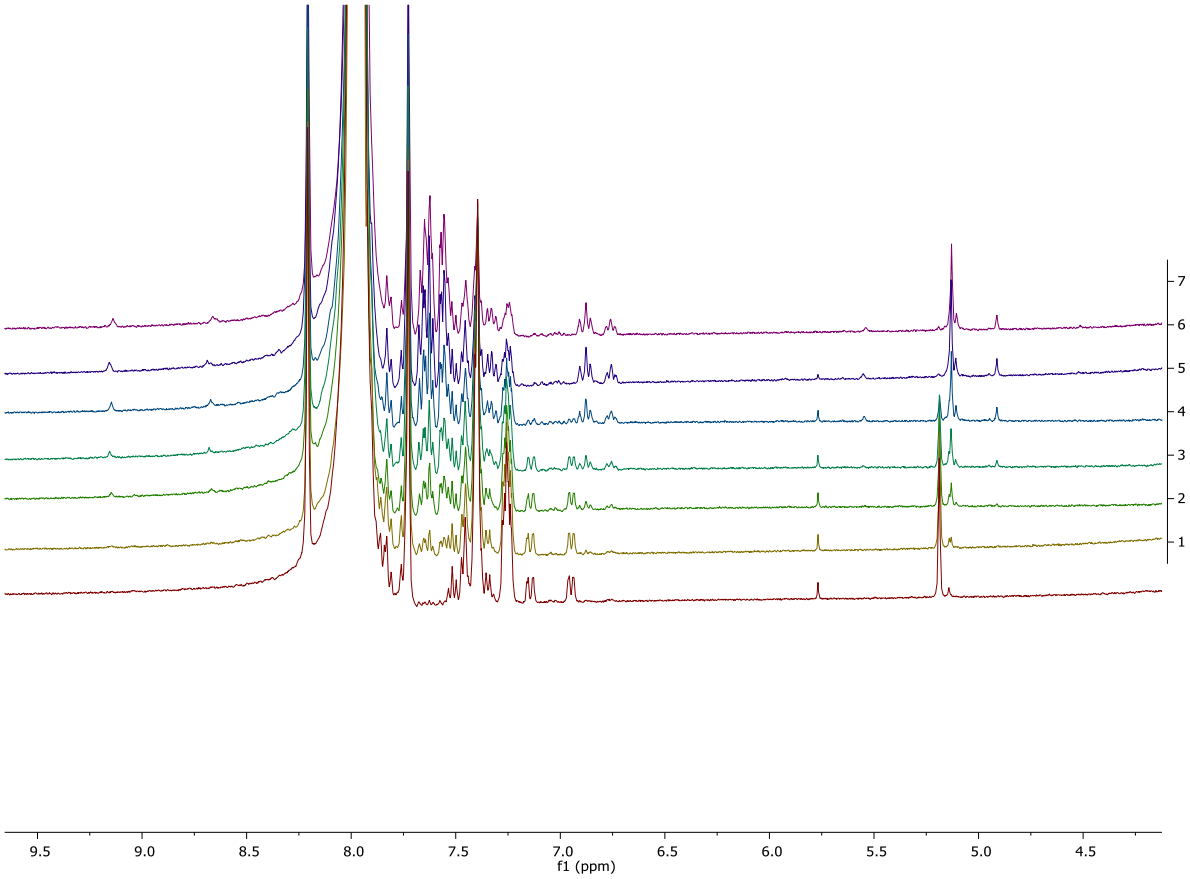
After 0, 2, 3, 4, 6, 10, 20 minutes starting from bottom.

NMR degradation standard conditions



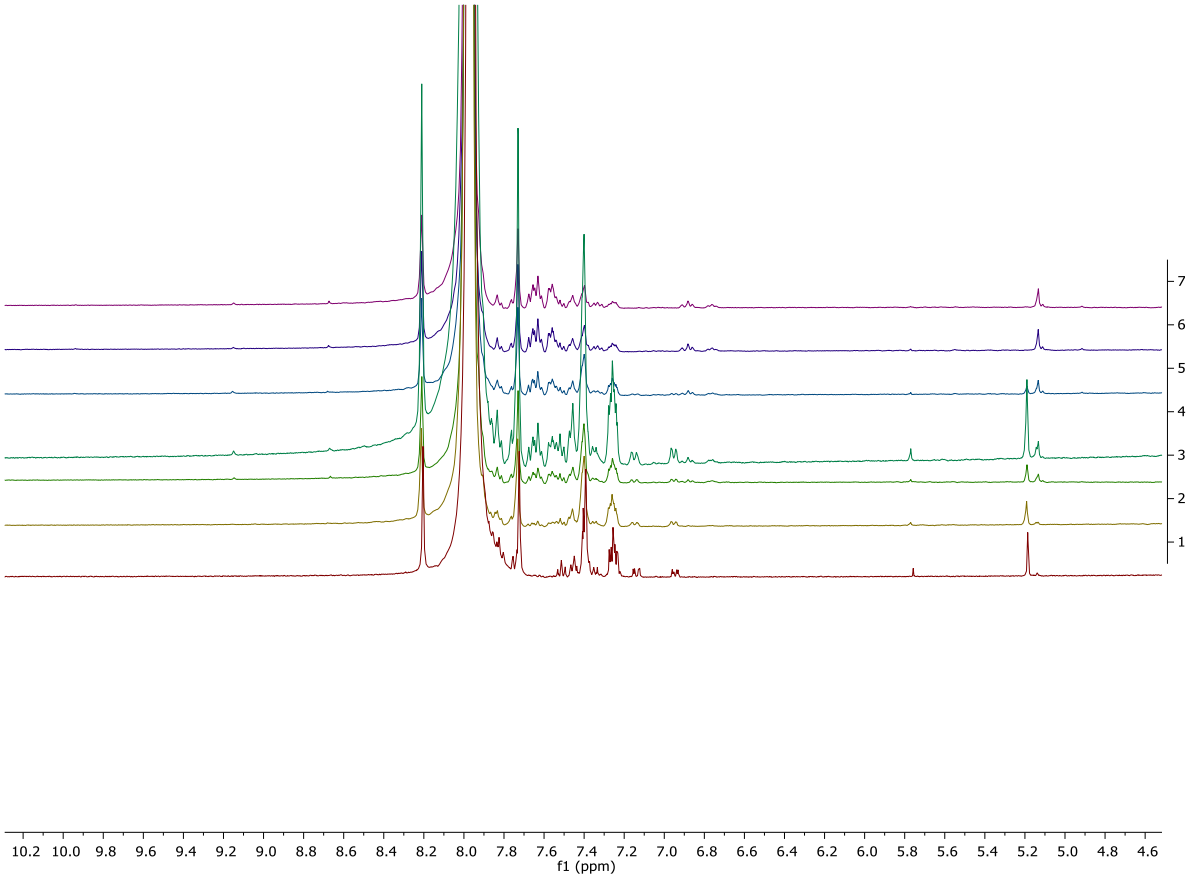
After 0, 2, 3, 4, 6, 10, 20 minutes starting from bottom.

NMR degradation standard conditions + 100mol% PPh_3



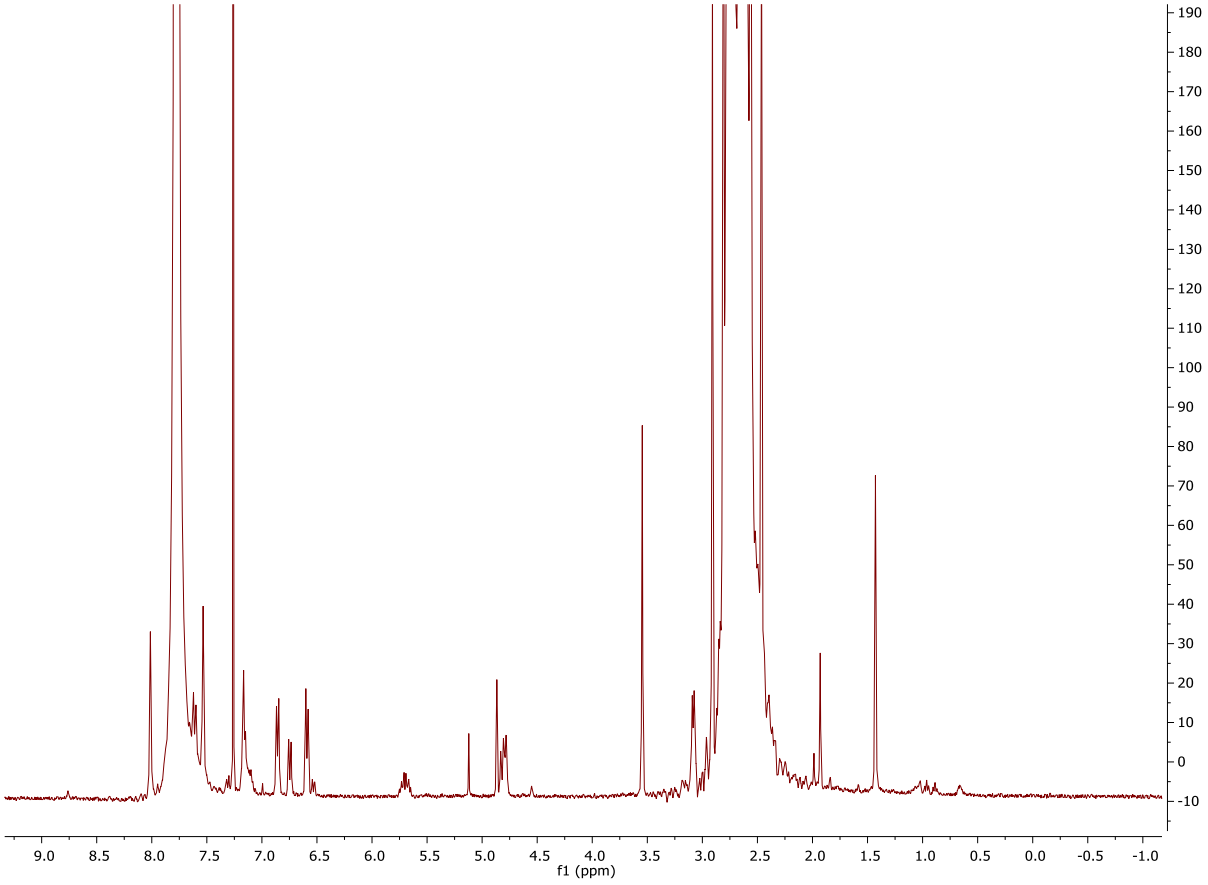
After 0, 2, 3, 4, 6, 10, 20 minutes starting from bottom.

NMR degradation standard conditions + 100mol% PPh_3



After 0, 2, 3, 4, 6, 10, 20 minutes starting from bottom.

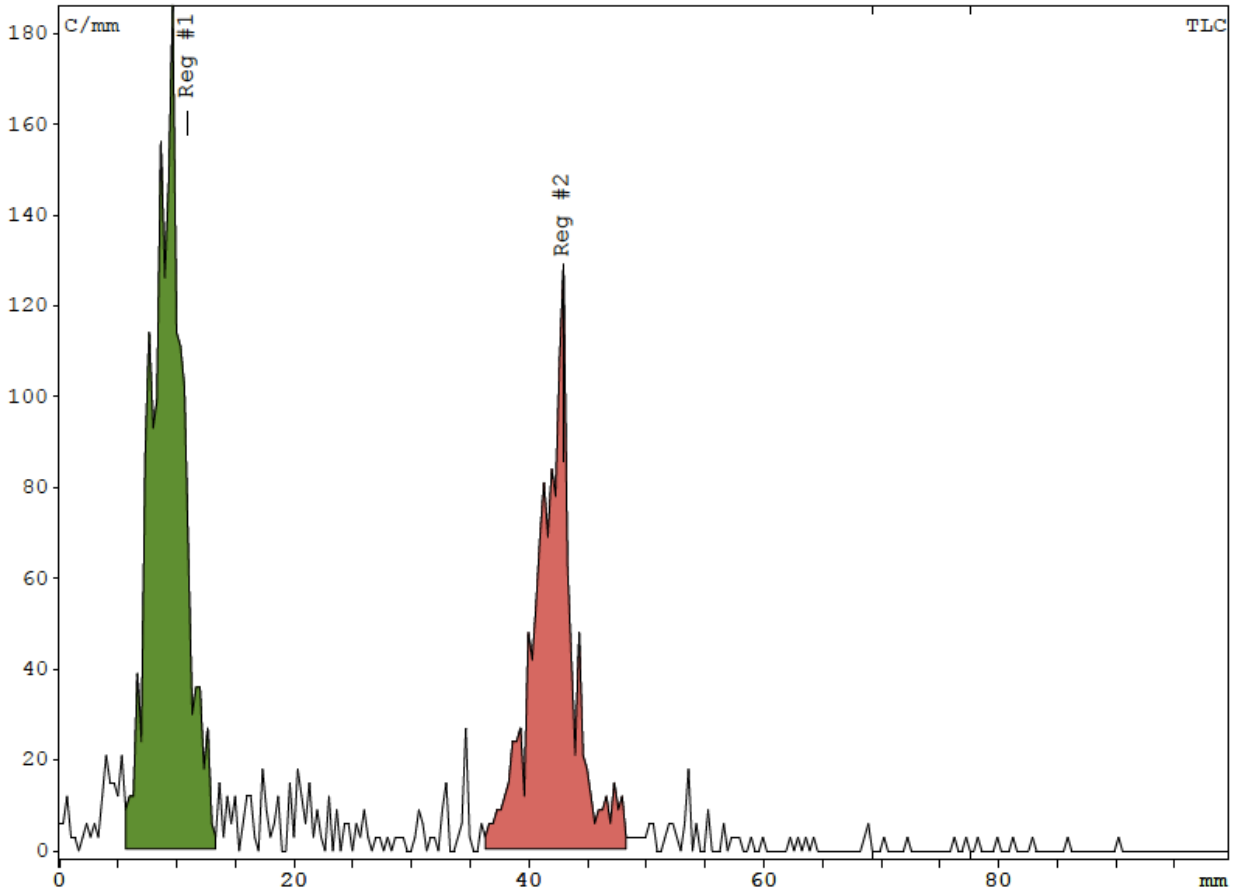
Alkene migration experiment



11. Radio TLC data

11.1 Ligand screening:

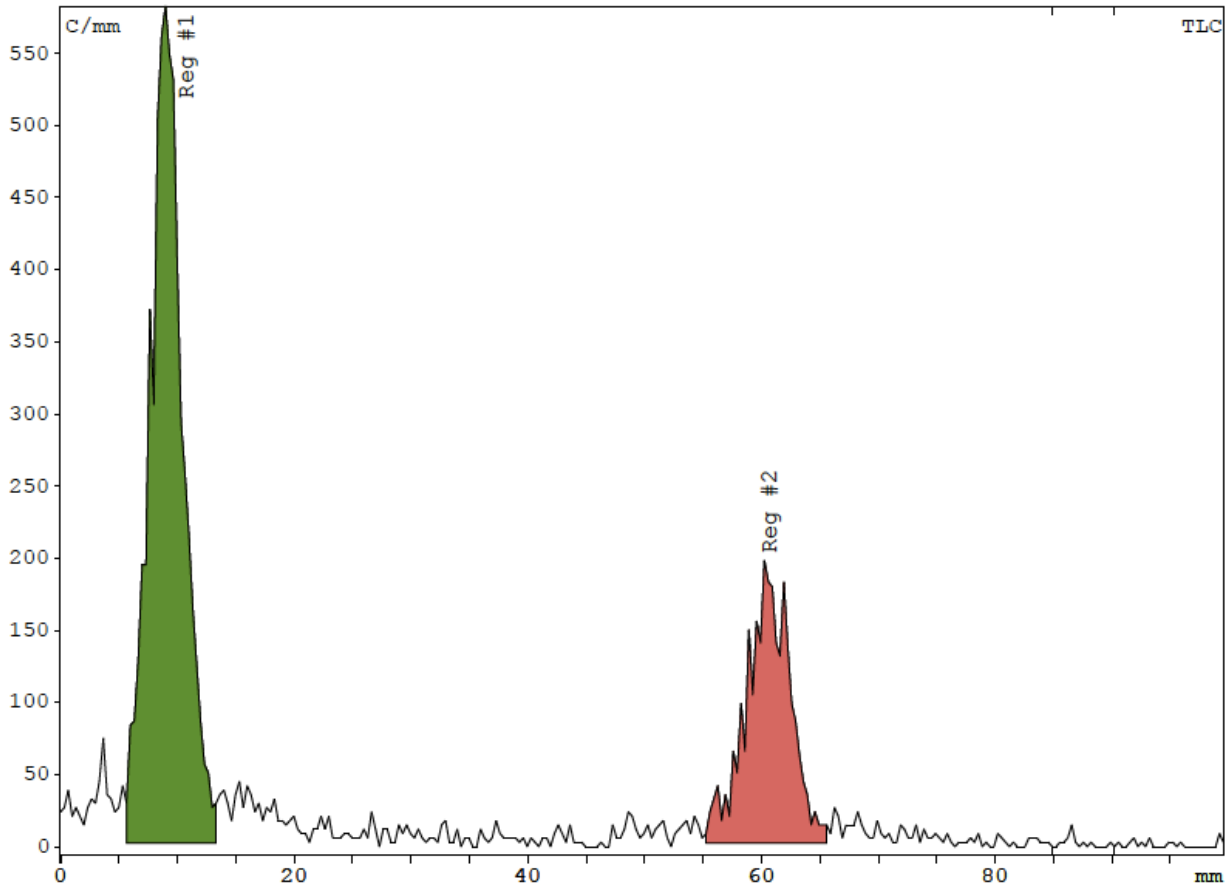
Entry 1:



Integration TLC

Substance	R/F	%Total	Type	Area	%Area
		%		Counts	%
Reg #1	0,093	48,13	DD	546,3200	57,84
Reg #2	0,423	35,08	DD	398,2400	42,16
Sum in ROI				944,5600	
Total area				1135,1600	
Area RF				1135,0000	
BKG1				0,48060	

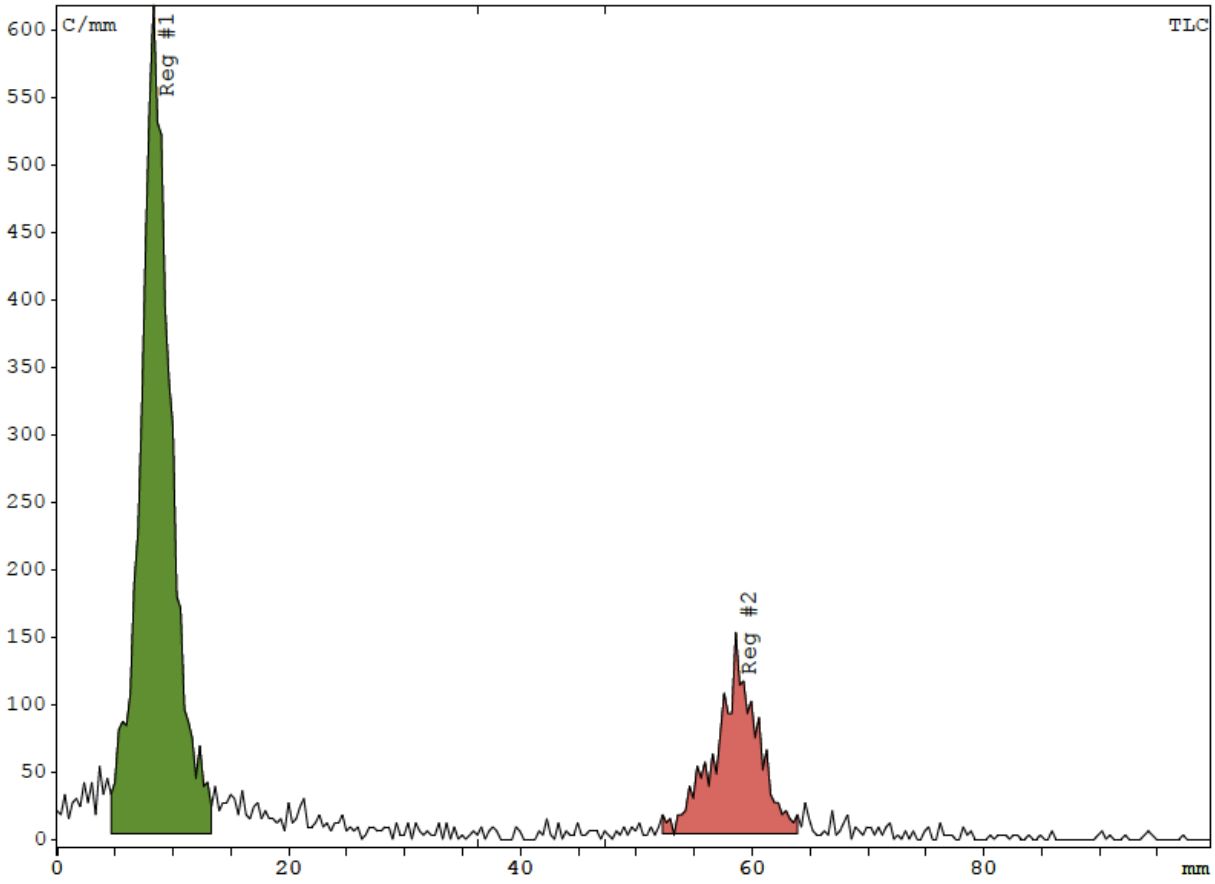
Entry 2:



Integration TLC

Substance	R/F	%Total	Type	Area	%Area
		%		Counts	%
Reg #1	0,090	56,74	DD	1918,313	69,75
Reg #2	0,603	24,60	DD	831,813	30,25
Sum in ROI				2750,125	
Total area				3381,063	
Area RF				3383,250	
BKG1				2,4405	

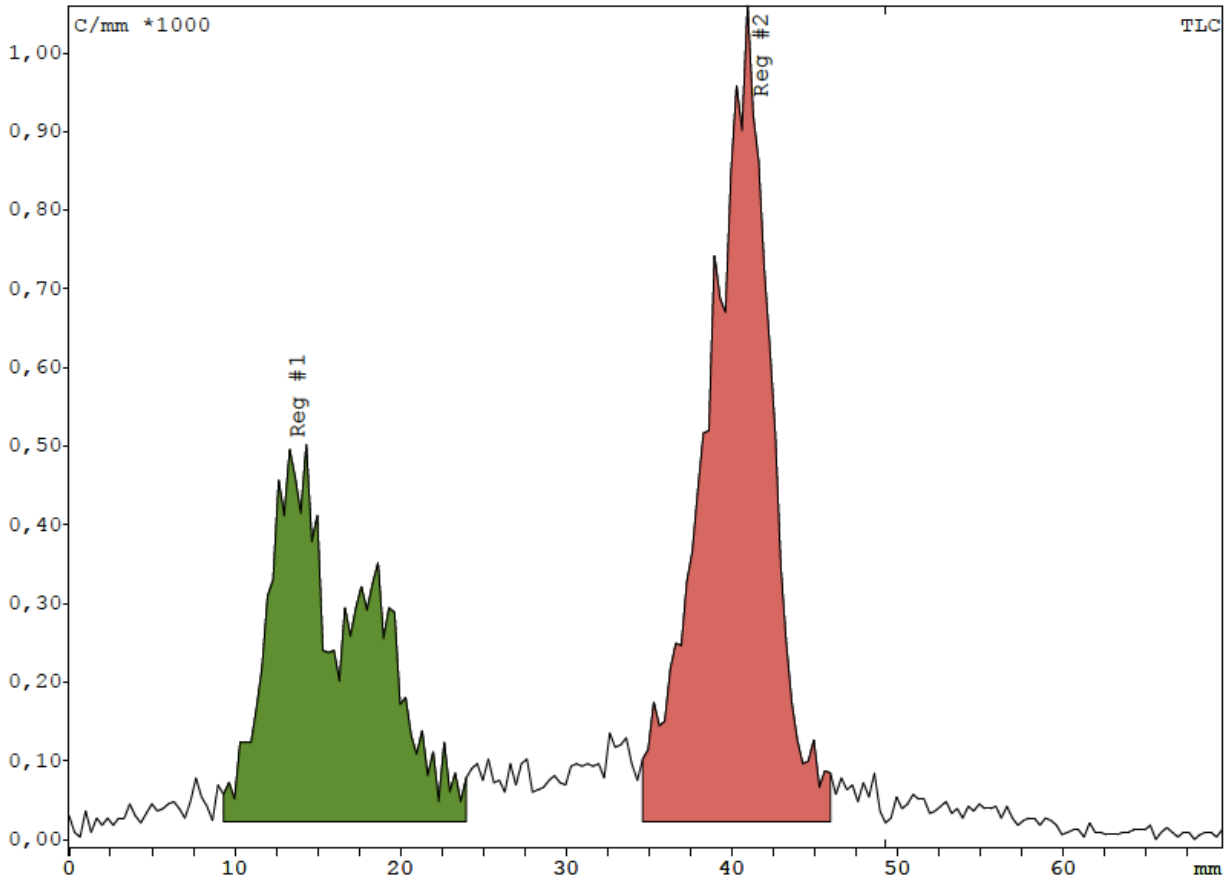
Entry 3:



Integration TLC

Substance	R/F	%Total	Type	Area	%Area
		%		Counts	%
Reg #1	0,083	68,17	DD	1856,545	76,38
Reg #2	0,593	21,09	DD	574,273	23,62
Sum in ROI				2430,818	
Total area				2723,273	
Area RF				2721,909	
BKG1				4,0960	

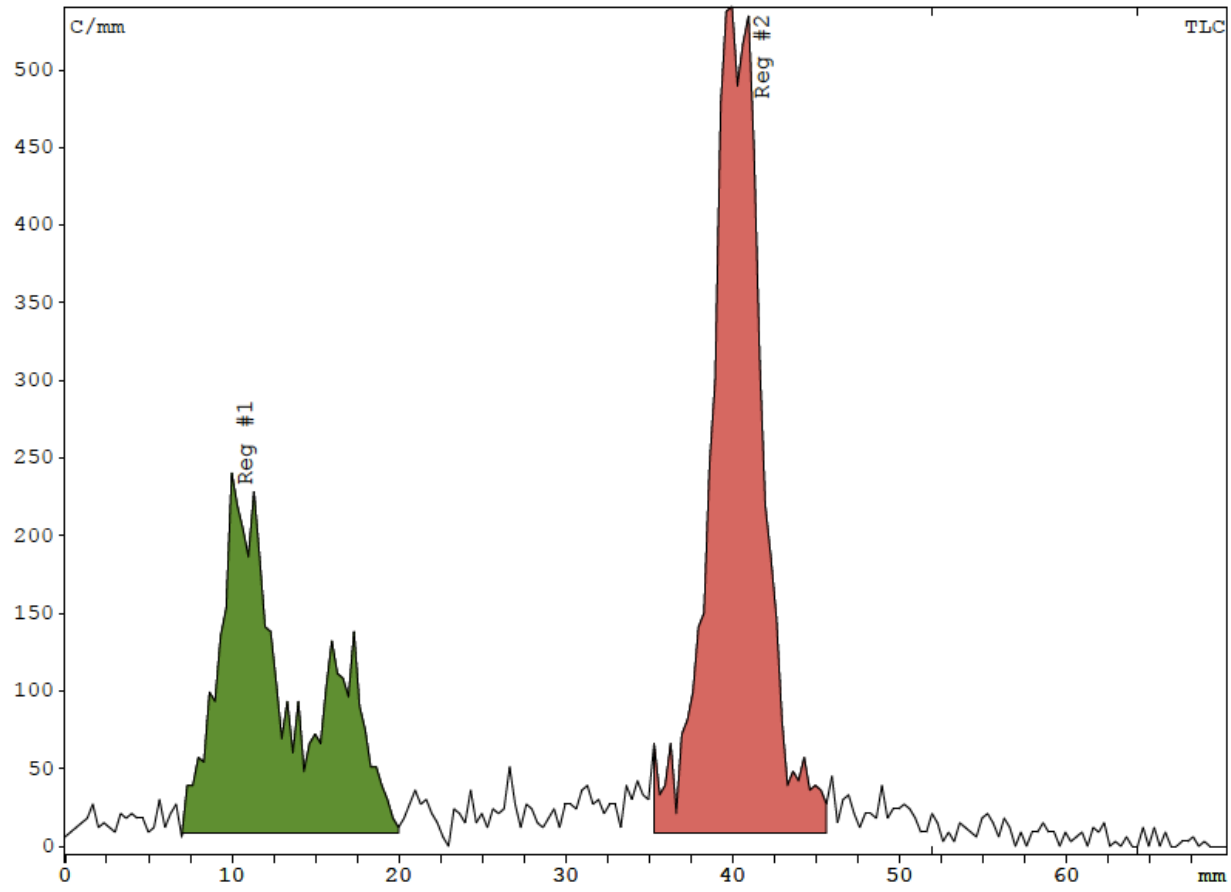
Entry 4:



Integration TLC

Substance	R/F	%Total	Type	Area	%Area
		%		Counts	%
Reg #1	0,195	35,94	DD	3097,548	40,43
Reg #2	0,586	52,95	DD	4563,742	59,57
Sum in ROI				7661,290	
Total area				8619,355	
Area RF				8612,935	
BKG1				22,2857	

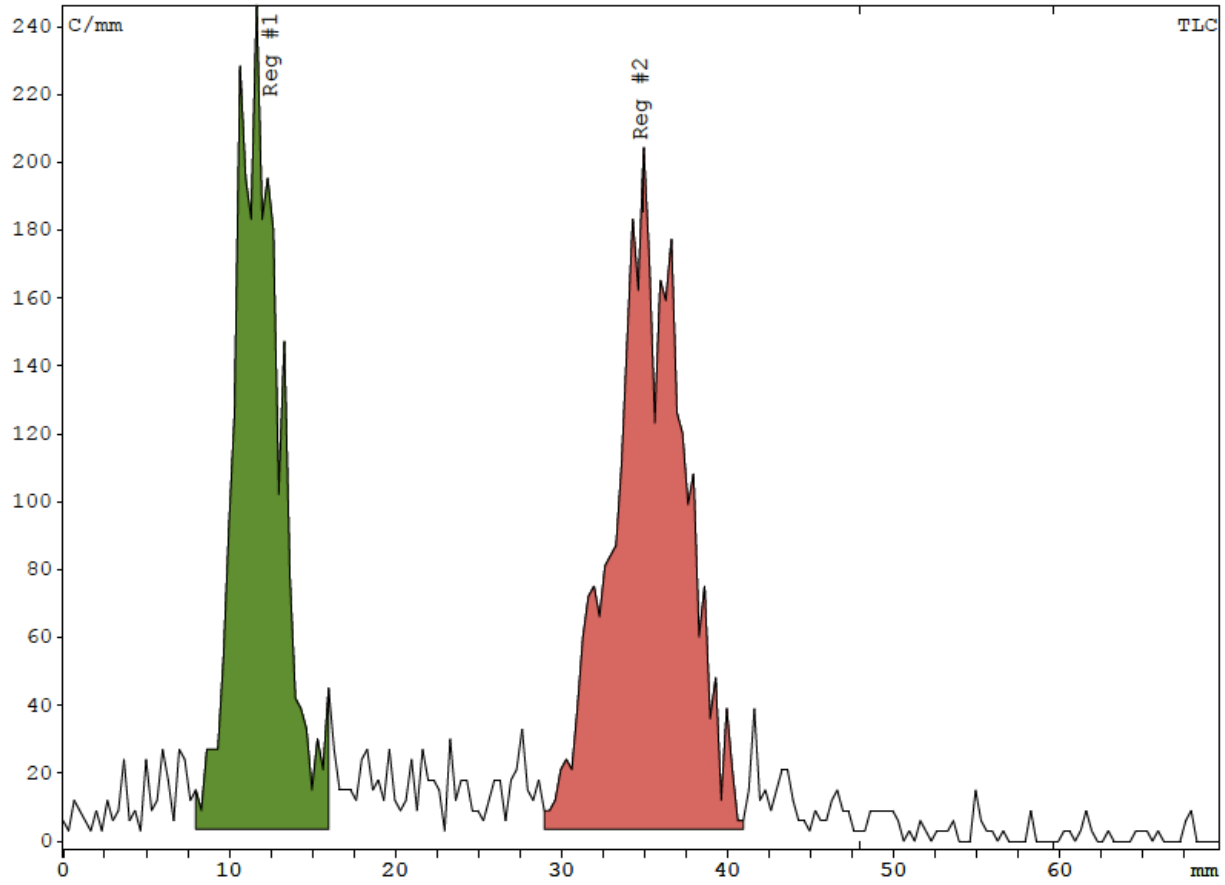
Entry 5:



Integration TLC

Substance	R/F	%Total	Type	Area	%Area
		%		Counts	%
Reg #1	0,152	34,33	DD	1199,324	38,17
Reg #2	0,576	55,61	DD	1943,027	61,83
Sum in ROI				3142,351	
Total area				3493,892	
Area RF				3491,054	
BKG1				8,5241	

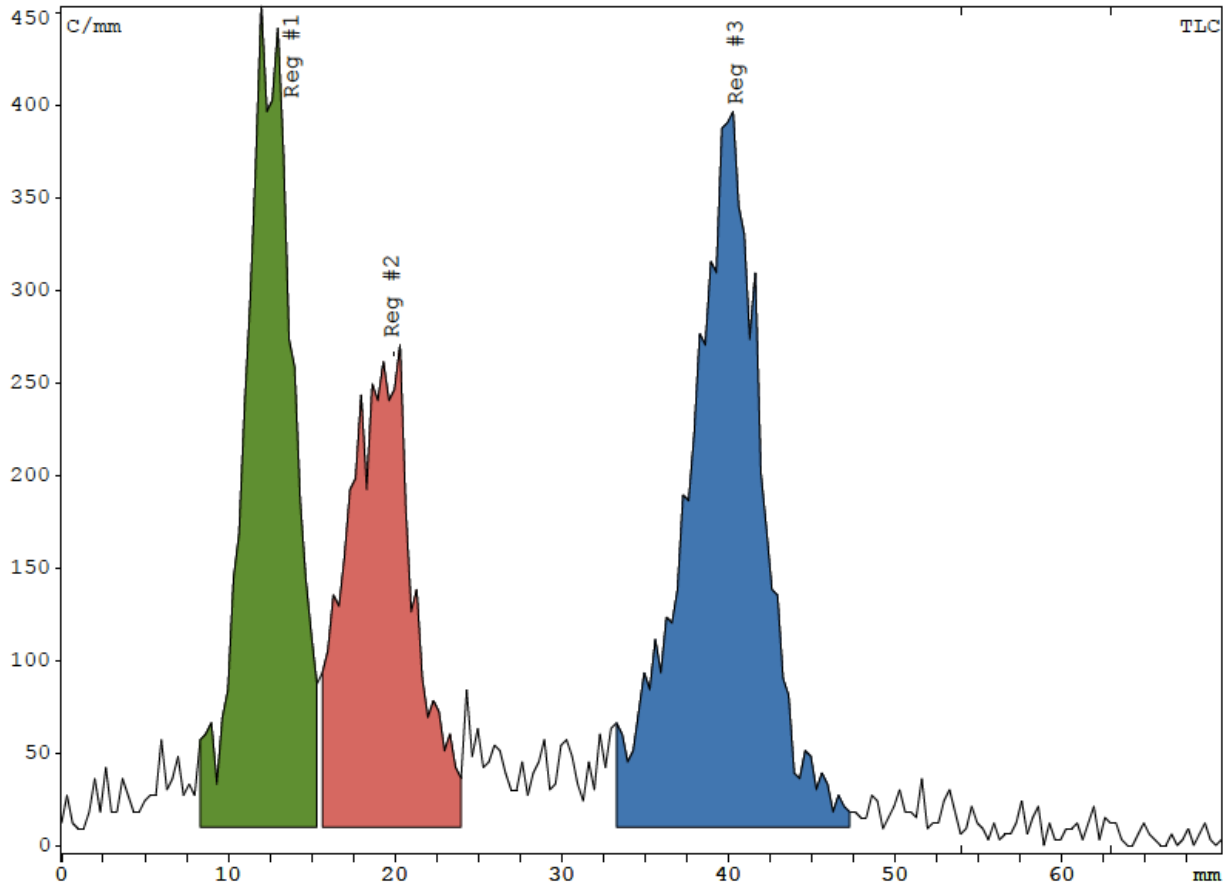
Entry 6:



Integration TLC

Substance	R/F	%Total	Type	Area	%Area
		%		Counts	%
Reg #1	0,162	37,18	DD	736,8857	43,38
Reg #2	0,495	48,52	DD	961,8286	56,62
Sum in ROI				1698,7143	
Total area				1982,1714	
Area RF				1981,0000	
BKG1				3,51865	

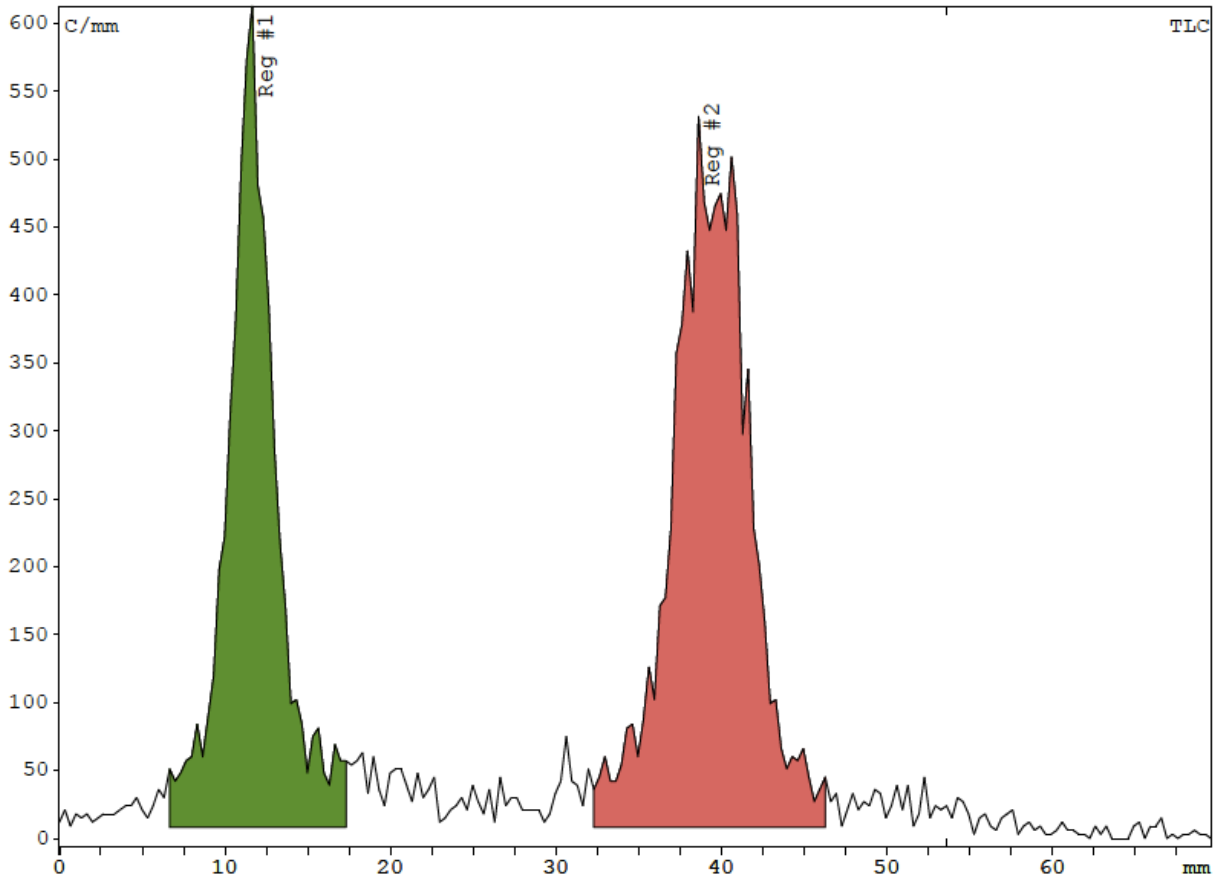
Entry 7:



Integration TLC

Substance	R/F	%Total	Type	Area	%Area
		%		Counts	%
Reg #1	0,181	28,34	DD	1469,778	31,46
Reg #2	0,281	23,21	DD	1203,593	25,76
Reg #3	0,576	38,54	DD	1998,556	42,78
Sum in ROI				4671,926	
Total area				5186,074	
Area RF				5182,778	
BKG1				9,9012	

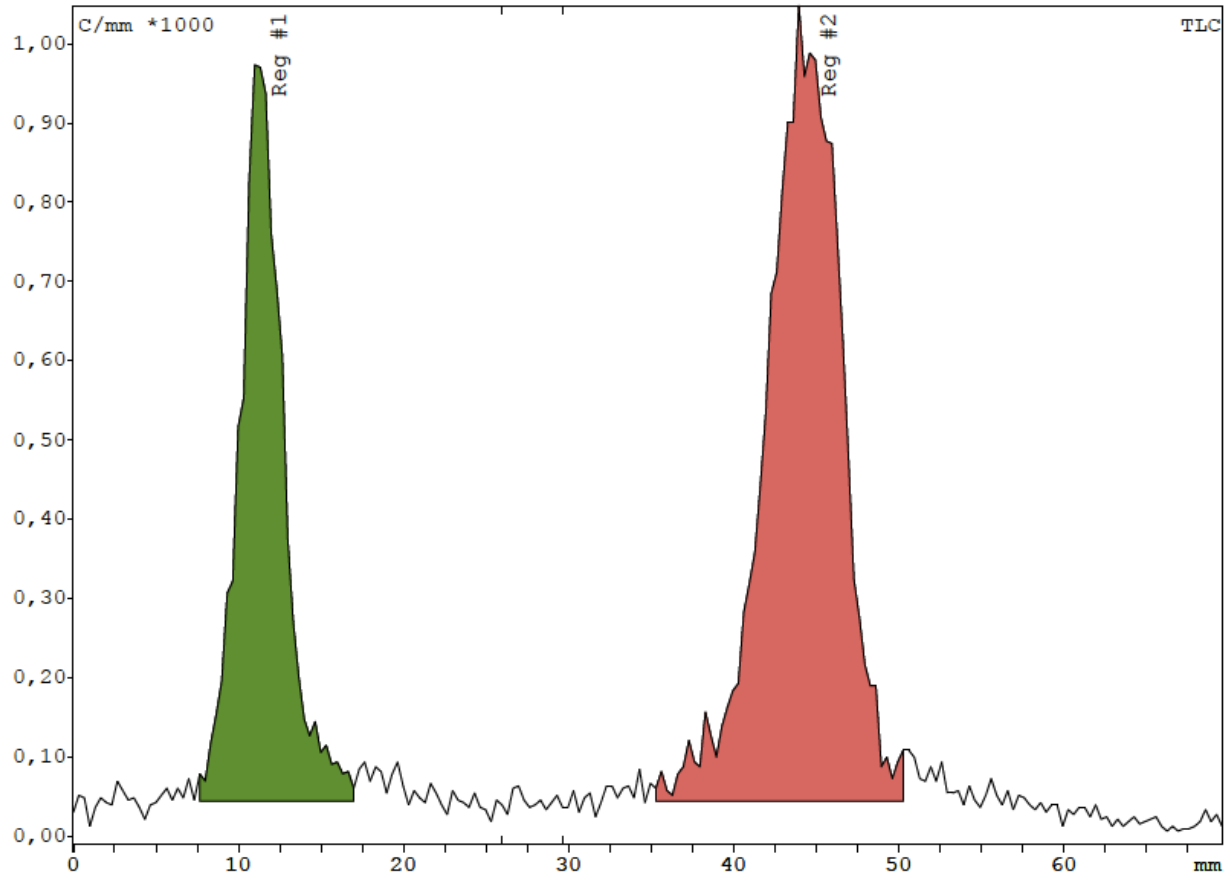
Entry 8:



Integration TLC

Substance	R/F	%Total	Type	Area	%Area
		%		Counts	%
Reg #1	0,167	36,73	DD	1950,143	41,53
Reg #2	0,562	51,73	DD	2746,000	58,47
Sum in ROI				4696,143	
Total area				5308,714	
Area RF				5307,000	
BKG1				8,1530	

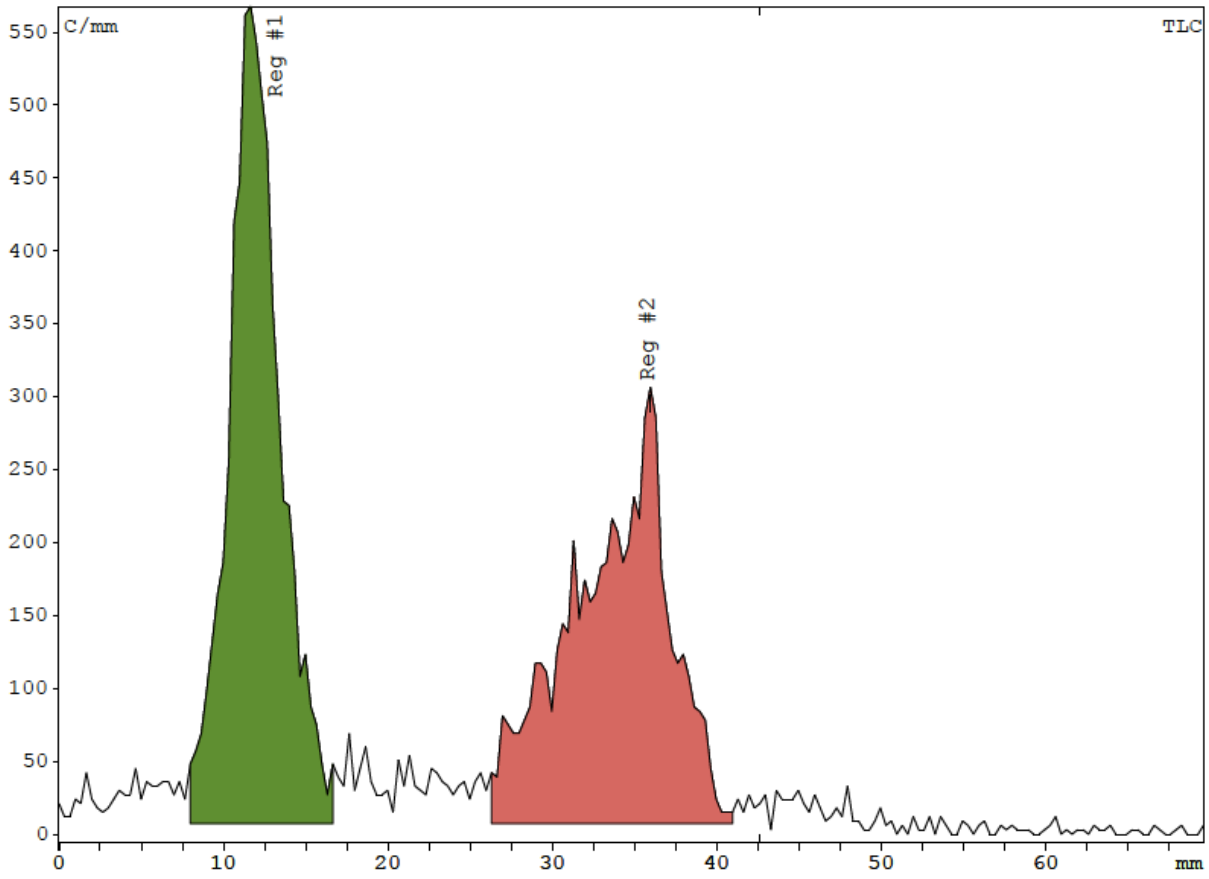
Entry 9:



Integration TLC

Substance	R/F	%Total	Type	Area	%Area
		%		Counts	%
Reg #1	0,162	35,17	DD	2889,727	35,47
Reg #2	0,638	63,98	DD	5256,455	64,53
Sum in ROI				8146,182	
Total area				8216,000	
Area RF				8210,455	
BKG1				43,6905	

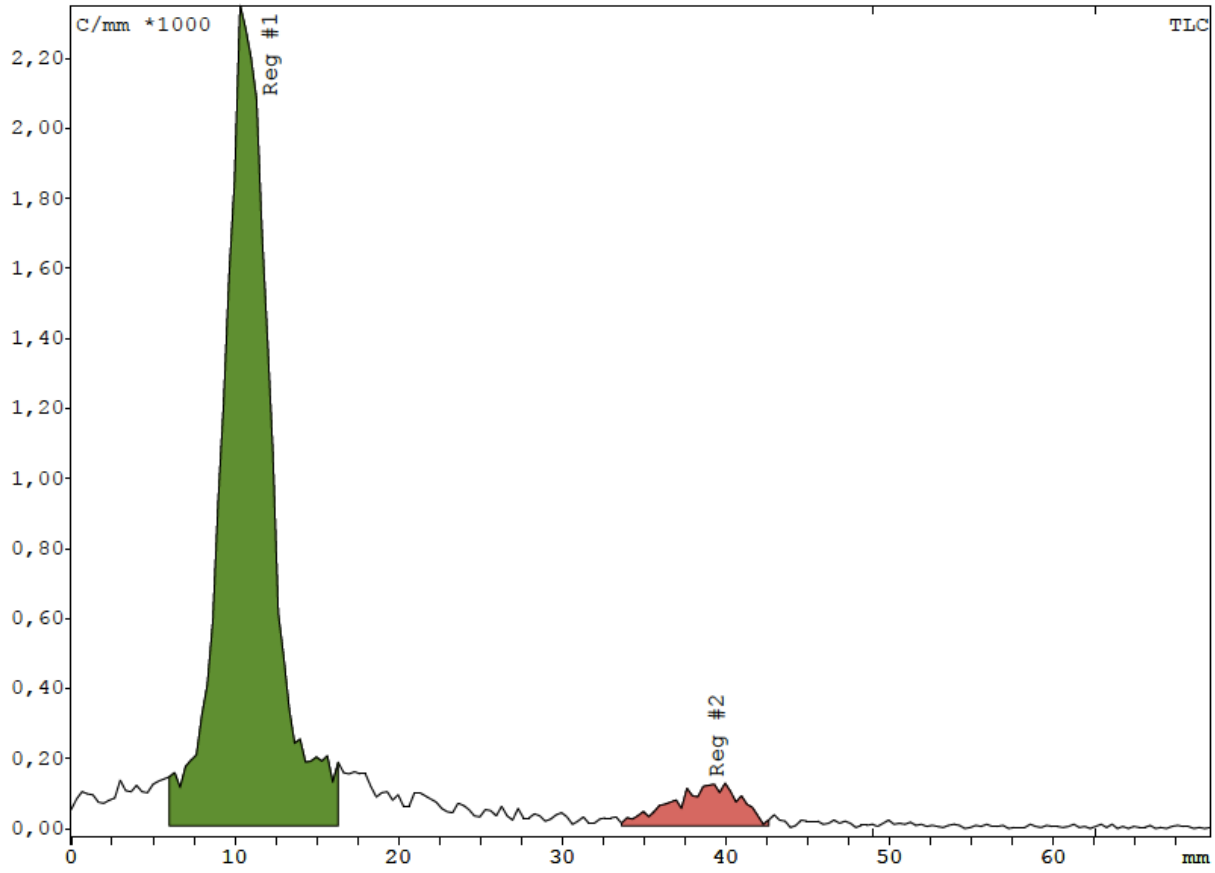
Entry 10:



Integration TLC

Substance	R/F	%Total	Type	Area	%Area
		%		Counts	%
Reg #1	0,171	46,73	DD	2035,220	52,35
Reg #2	0,510	42,54	DD	1852,756	47,65
Sum in ROI				3887,976	
Total area				4355,341	
Area RF				4352,927	
BKG1				7,2529	

Entry 11:

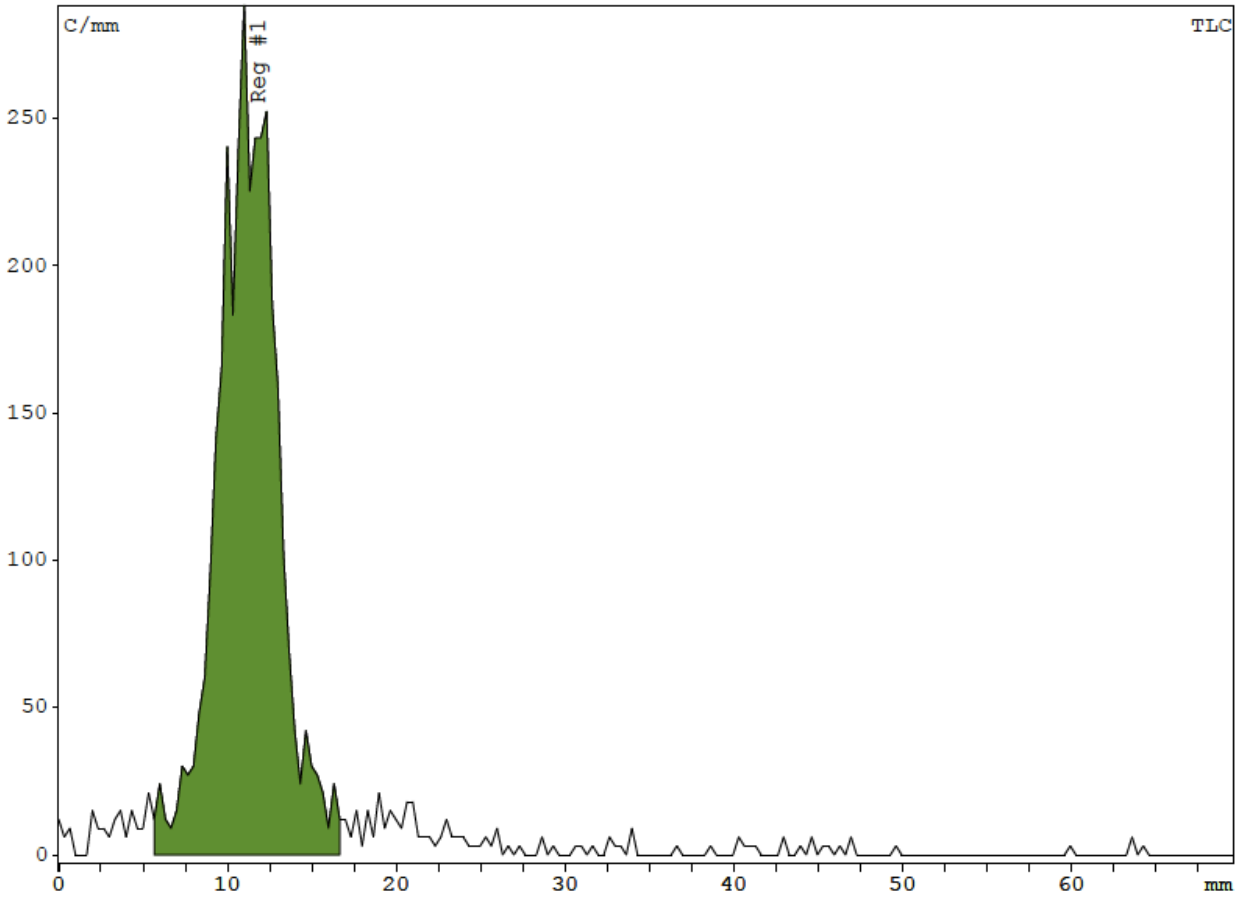


Integration TLC

Substance	R/F	%Total	Type	Area	%Area
		%		Counts	%
Reg #1	0,152	78,51	DD	7943,098	93,27
Reg #2	0,562	5,67	DD	573,537	6,73
Sum in ROI				8516,634	
Total area				10117,561	
Area RF				10114,951	
BKG1				7,8390	

Radio TLC kinetics

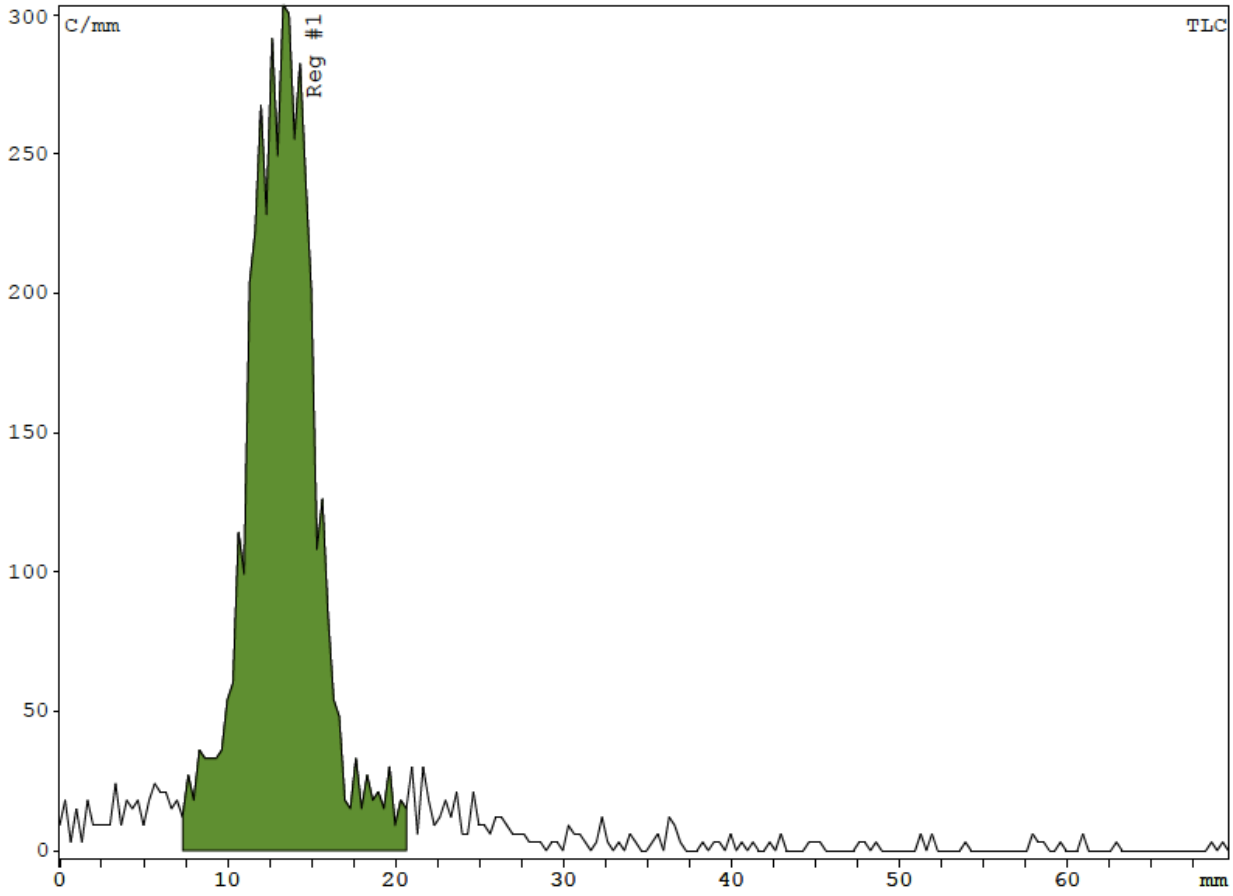
Standard procedure + 100 mol% PPh_3 + 1 min N_2 starting point:



Integration TLC

Substance	R/F	%Total	Type	Area	%Area
		%		Counts	%
Reg #1	0,167	86,47	DD	1106,000	100,00
Sum in ROI				1106,000	
Total area				1279,000	
Area RF				1279,000	

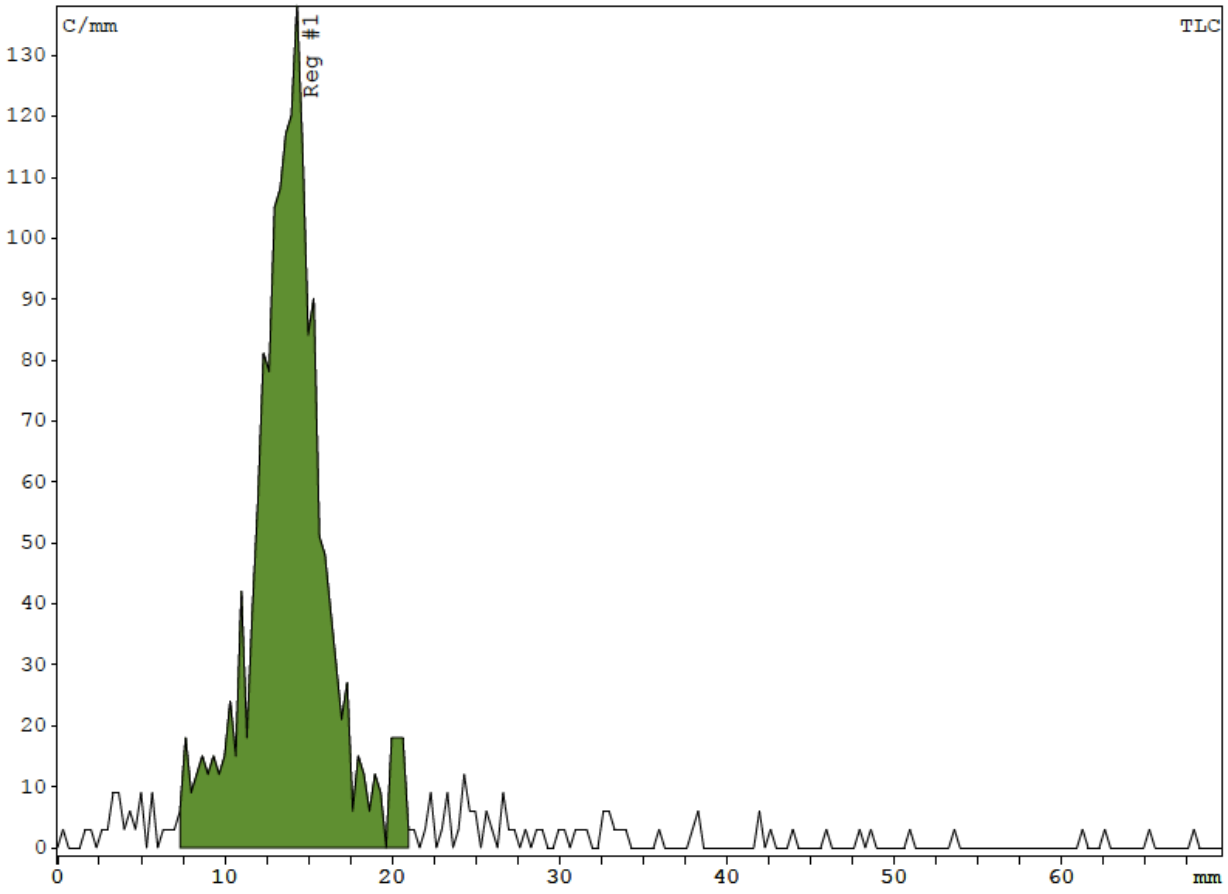
Standard procedure + 100 mol% PPh_3 + 1 min N_2 1 min:



Integration TLC

Substance	R/F	%Total	Type	Area	%Area
		%		Counts	%
Reg #1	0,190	84,35	DD	1412,000	100,00
Sum in ROI				1412,000	
Total area				1674,000	
Area RF				1675,000	

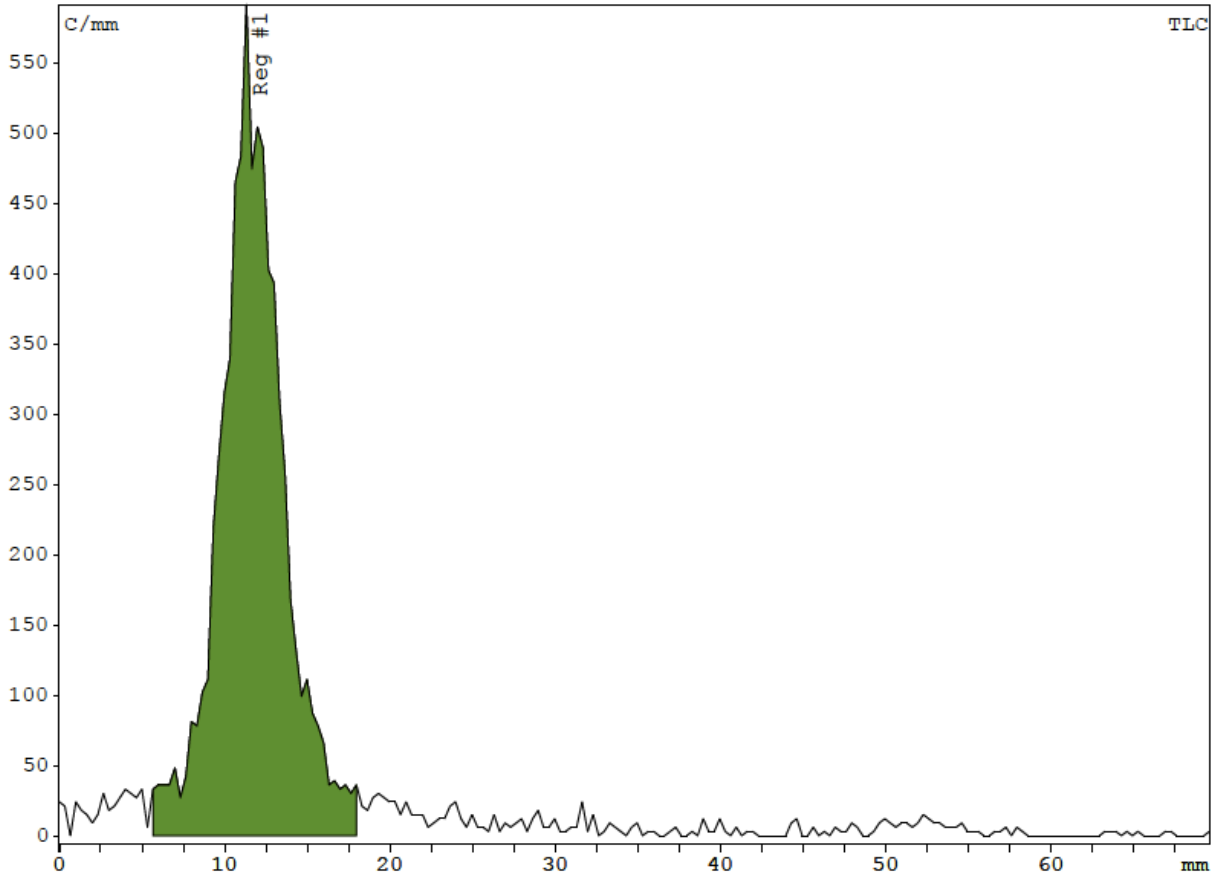
Standard procedure + 100 mol% PPh_3 + 1 min N_2 2 min:



Integration TLC

Substance	R/F	%Total	Type	Area	%Area
		%		Counts	%
Reg #1	0,200	87,05	DD	558,0000	100,00
Sum in ROI				558,0000	
Total area				641,0000	
Area RF				641,0000	

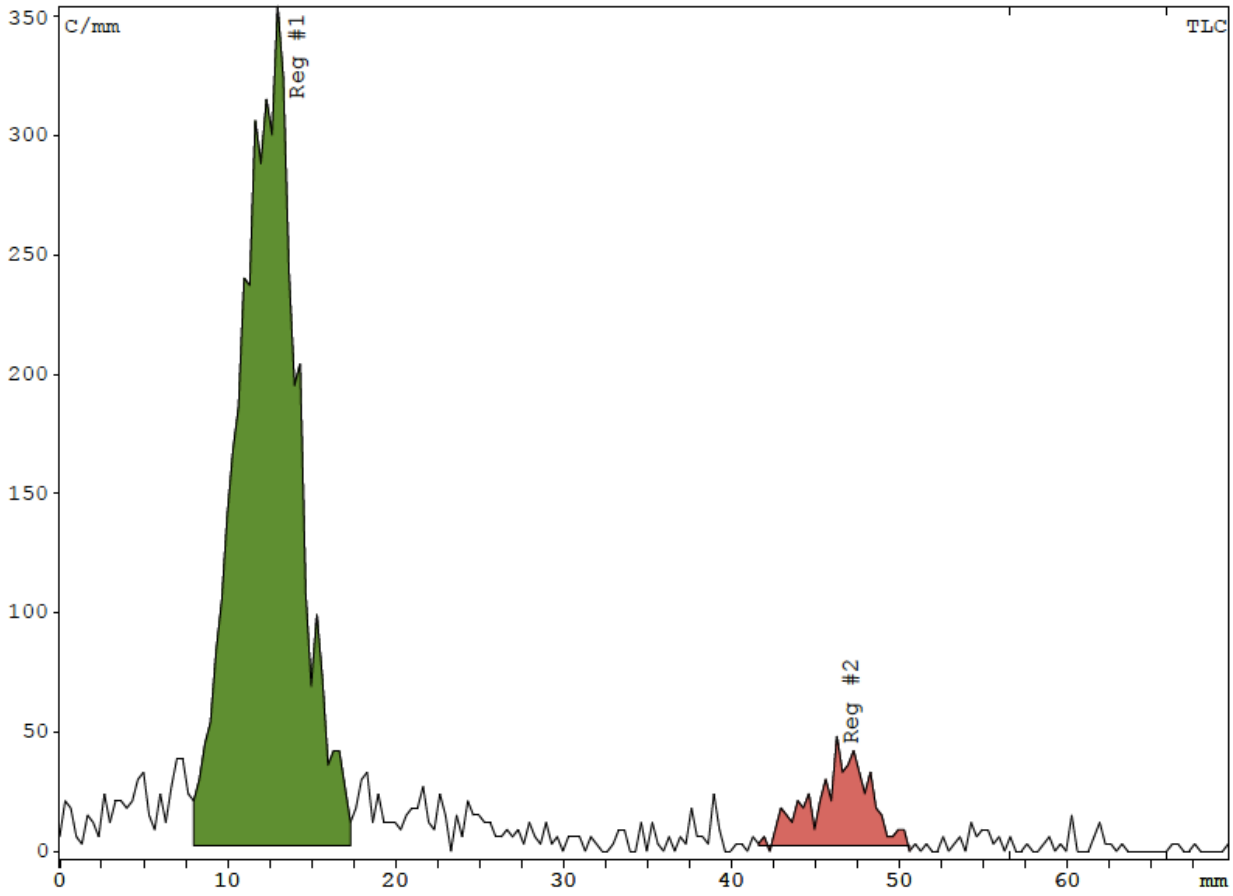
Standard procedure + 100 mol% PPh_3 + 1 min N_2 3 min:



Integration TLC

Substance	R/F	%Total	Type	Area	%Area
		%		Counts	%
Reg #1	0,167	84,48	DD	2352,000	100,00
Sum in ROI				2352,000	
Total area				2784,000	
Area RF				2784,000	

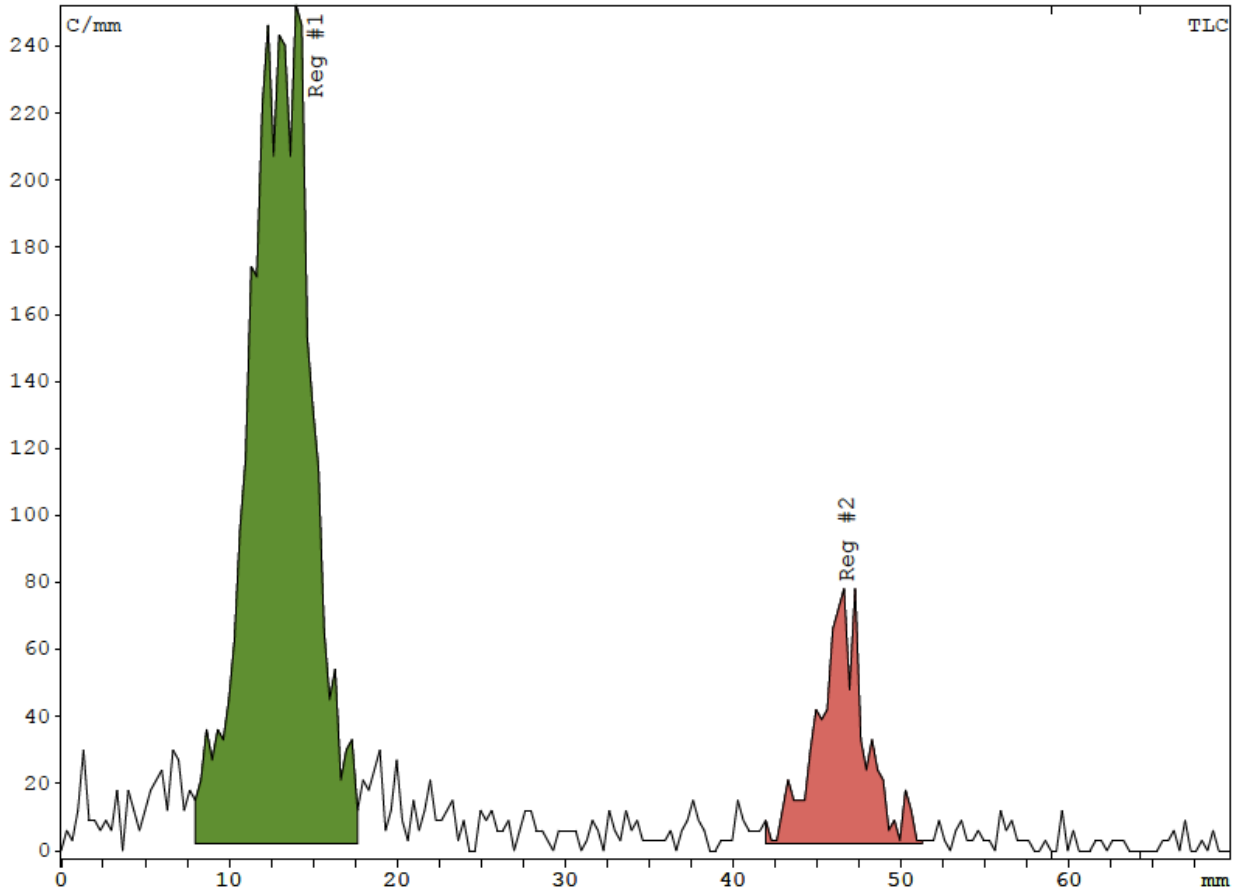
Standard procedure + 100 mol% PPh_3 + 1 min N_2 4 min:



Integration TLC

Substance	R/F	%Total	Type	Area	%Area
		%		Counts	%
Reg #1	0,181	75,82	DD	1424,000	90,31
Reg #2	0,671	8,13	DD	152,750	9,69
Sum in ROI				1576,750	
Total area				1878,250	
Area RF				1877,500	
BKG1				2,2528	

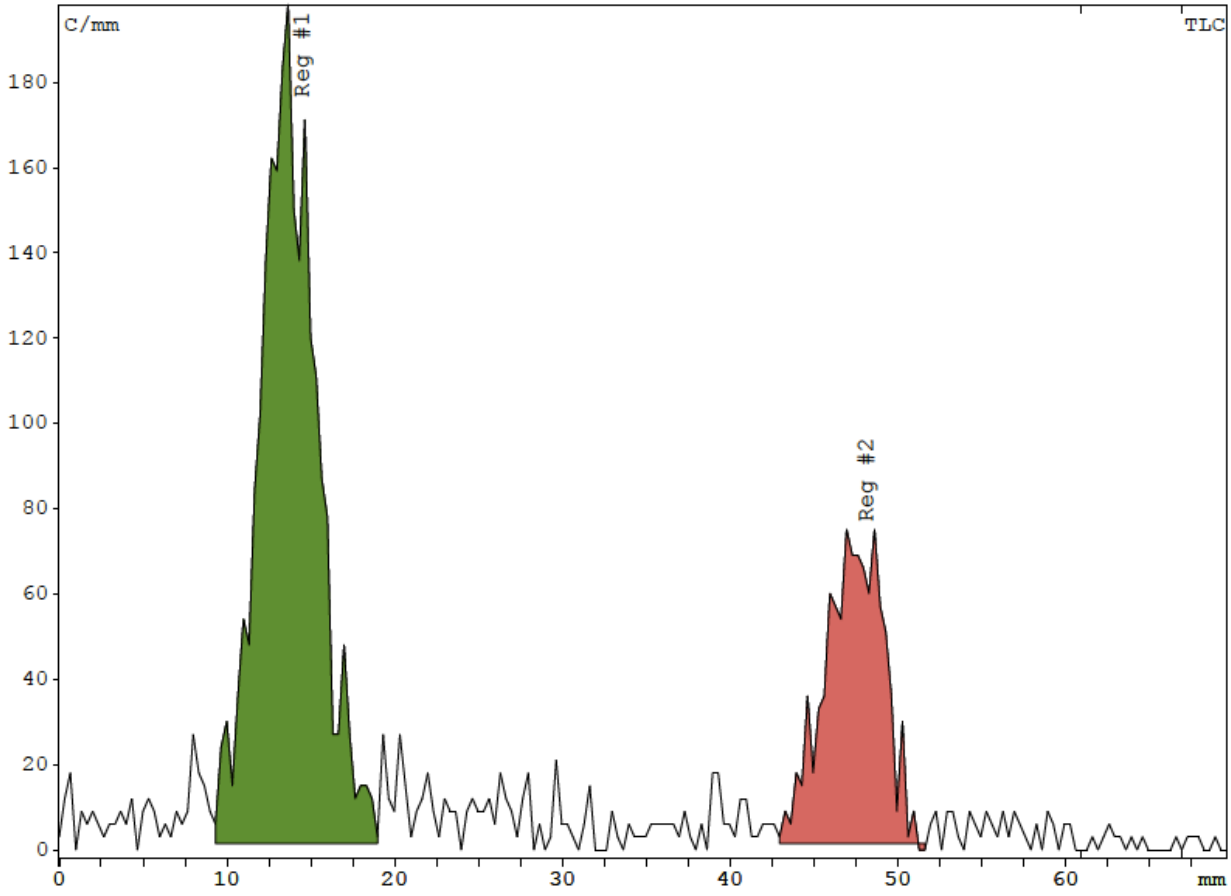
Standard procedure + 100 mol% PPh_3 + 1 min N_2 5 min:



Integration TLC

Substance	R/F	%Total	Type	Area	%Area
		%		Counts	%
Reg #1	0,195	69,29	DD	1095,063	82,10
Reg #2	0,667	15,11	DD	238,750	17,90
Sum in ROI				1333,813	
Total area				1580,313	
Area RF				1579,625	
BKG1				2,0651	

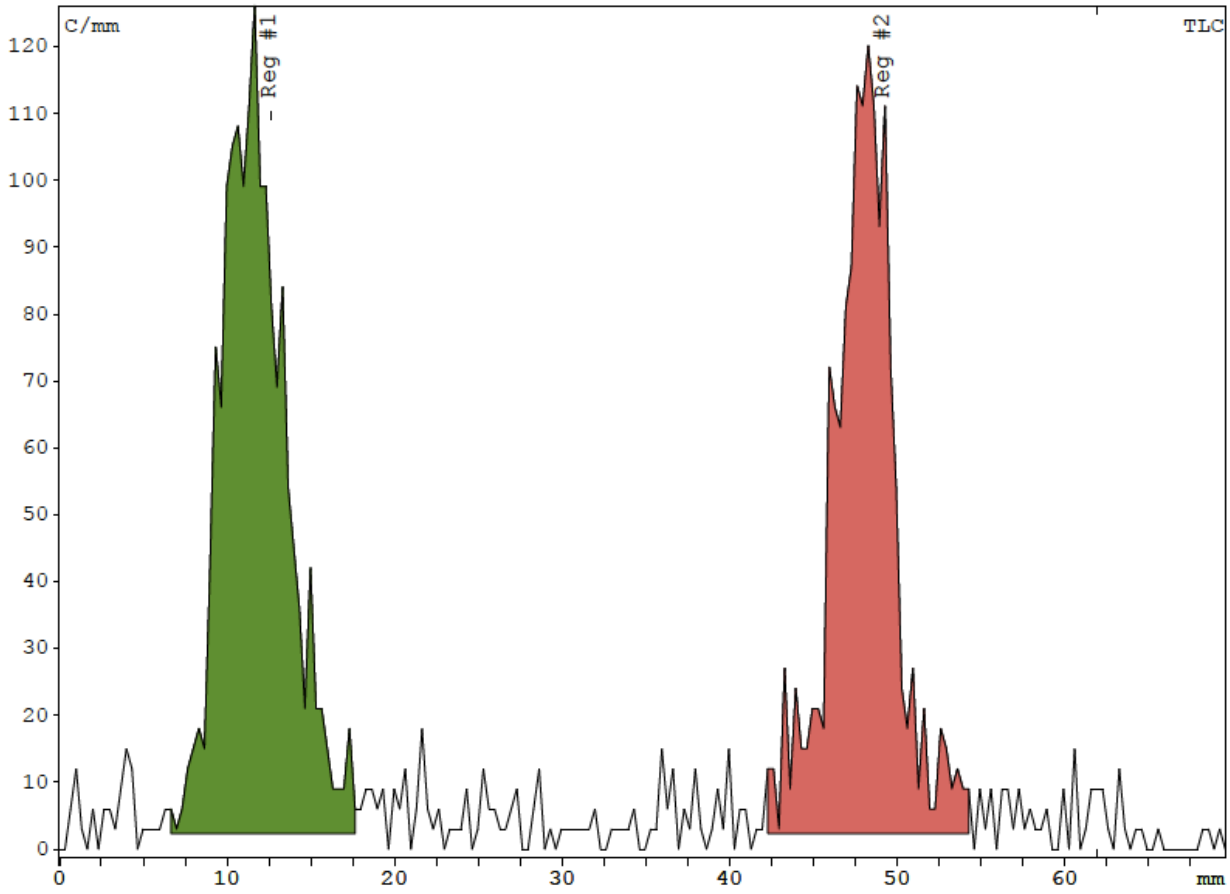
Standard procedure + 100 mol% PPh_3 + 1 min N_2 6 min:



Integration TLC

Substance	R/F	%Total	Type	Area	%Area
		%		Counts	%
Reg #1	0,190	57,56	DD	744,5000	70,94
Reg #2	0,686	23,58	DD	305,0000	29,06
Sum in ROI				1049,5000	
Total area				1293,5000	
Area RF				1293,0000	
BKG1				1,50186	

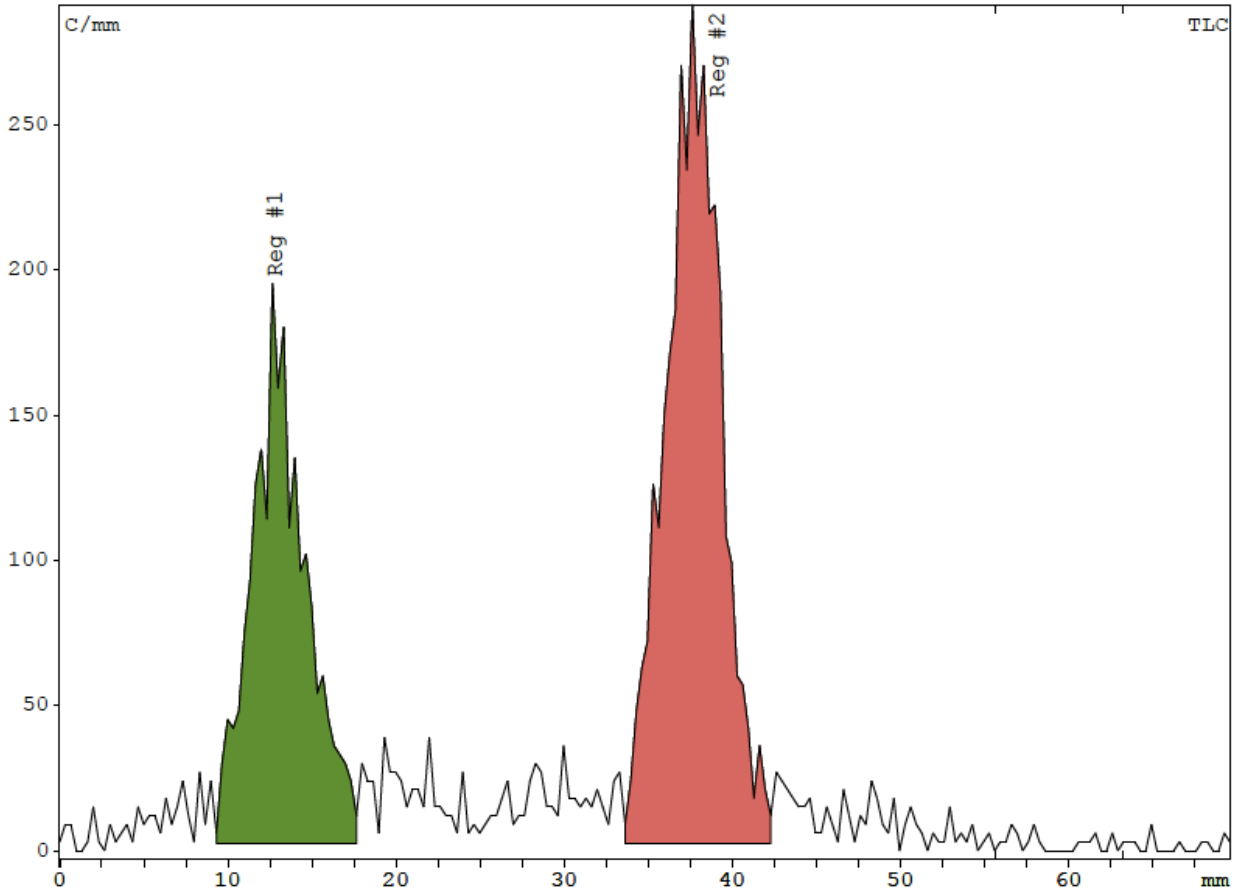
Standard procedure + 100 mol% PPh_3 + 1 min N_2 8 min:



Integration TLC

Substance	R/F	%Total	Type	Area	%Area
		%		Counts	%
Reg #1	0,157	47,70	DD	520,1739	52,33
Reg #2	0,690	43,45	DD	473,8261	47,67
Sum in ROI				994,0000	
Total area				1090,4348	
Area RF				1090,6522	
BKG1				2,35074	

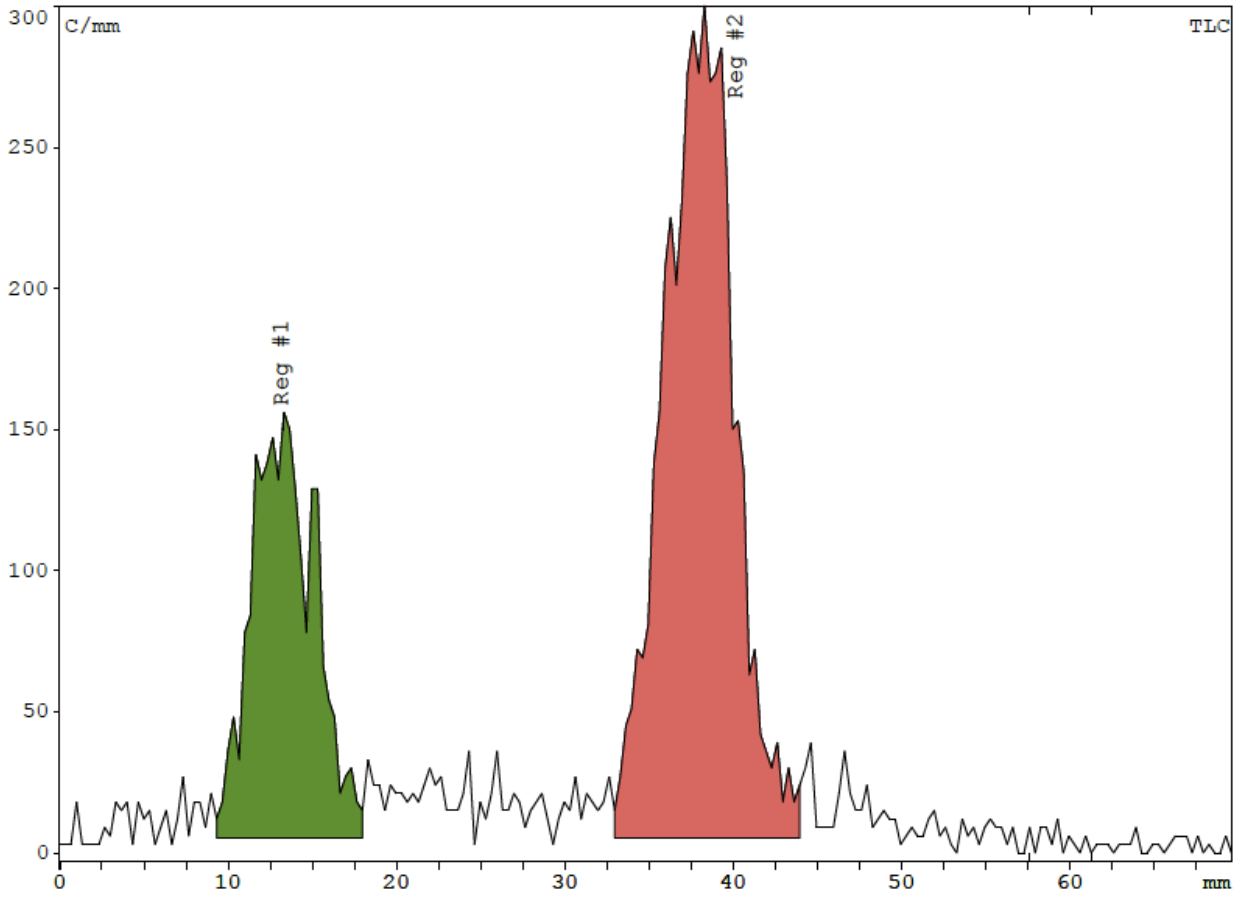
Standard procedure + 100 mol% PPh_3 + 1 min N_2 10 min:



Integration TLC

Substance	R/F	%Total	Type	Area	%Area
		%		Counts	%
Reg #1	0,181	30,56	DD	666,348	37,86
Reg #2	0,538	50,15	DD	1093,522	62,14
Sum in ROI				1759,870	
Total area				2180,348	
Area RF				2181,522	
BKG1				2,4813	

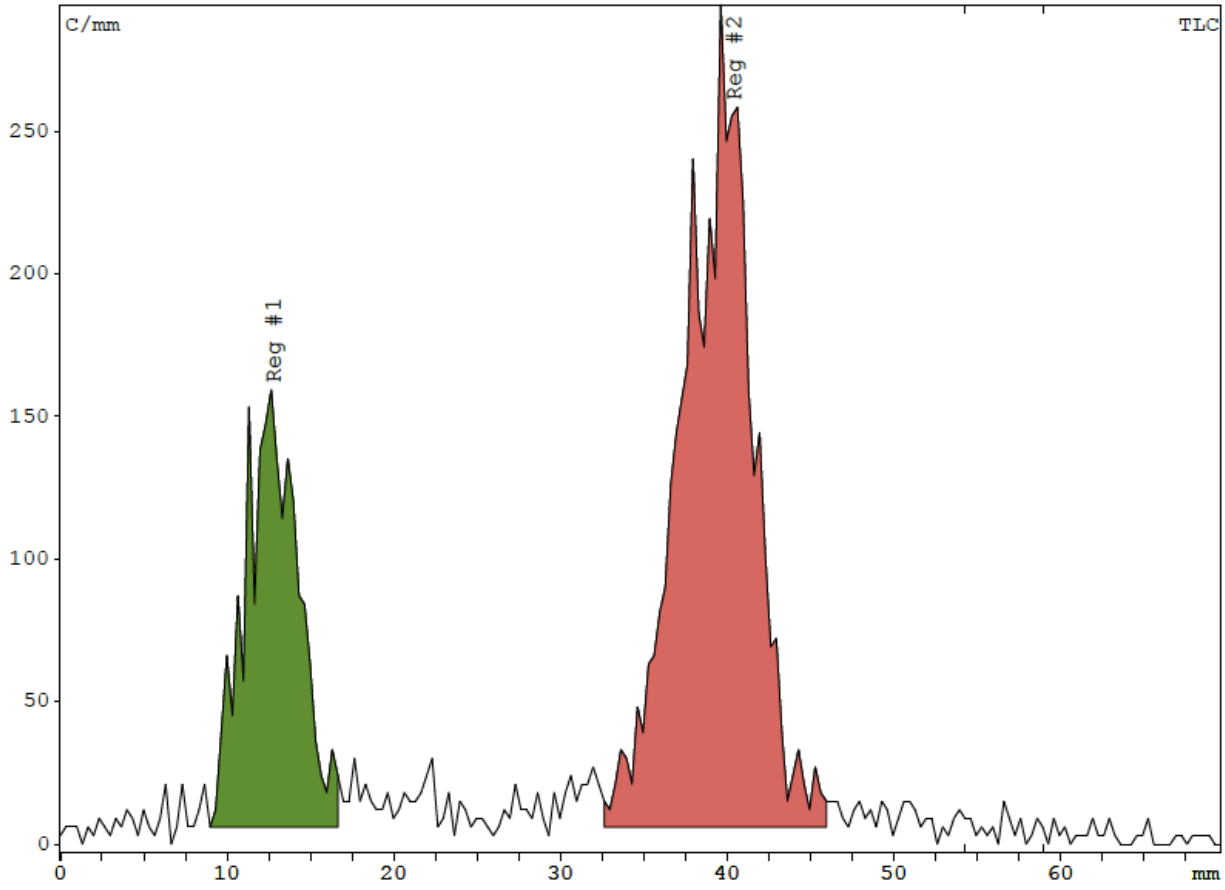
Standard procedure + 100 mol% PPh_3 + 1 min N_2 15 min:



Integration TLC

Substance	R/F	%Total	Type	Area	%Area
		%		Counts	%
Reg #1	0,186	27,34	DD	668,091	31,56
Reg #2	0,548	59,29	DD	1449,000	68,44
Sum in ROI				2117,091	
Total area				2444,000	
Area RF				2444,273	
BKG1				5,1883	

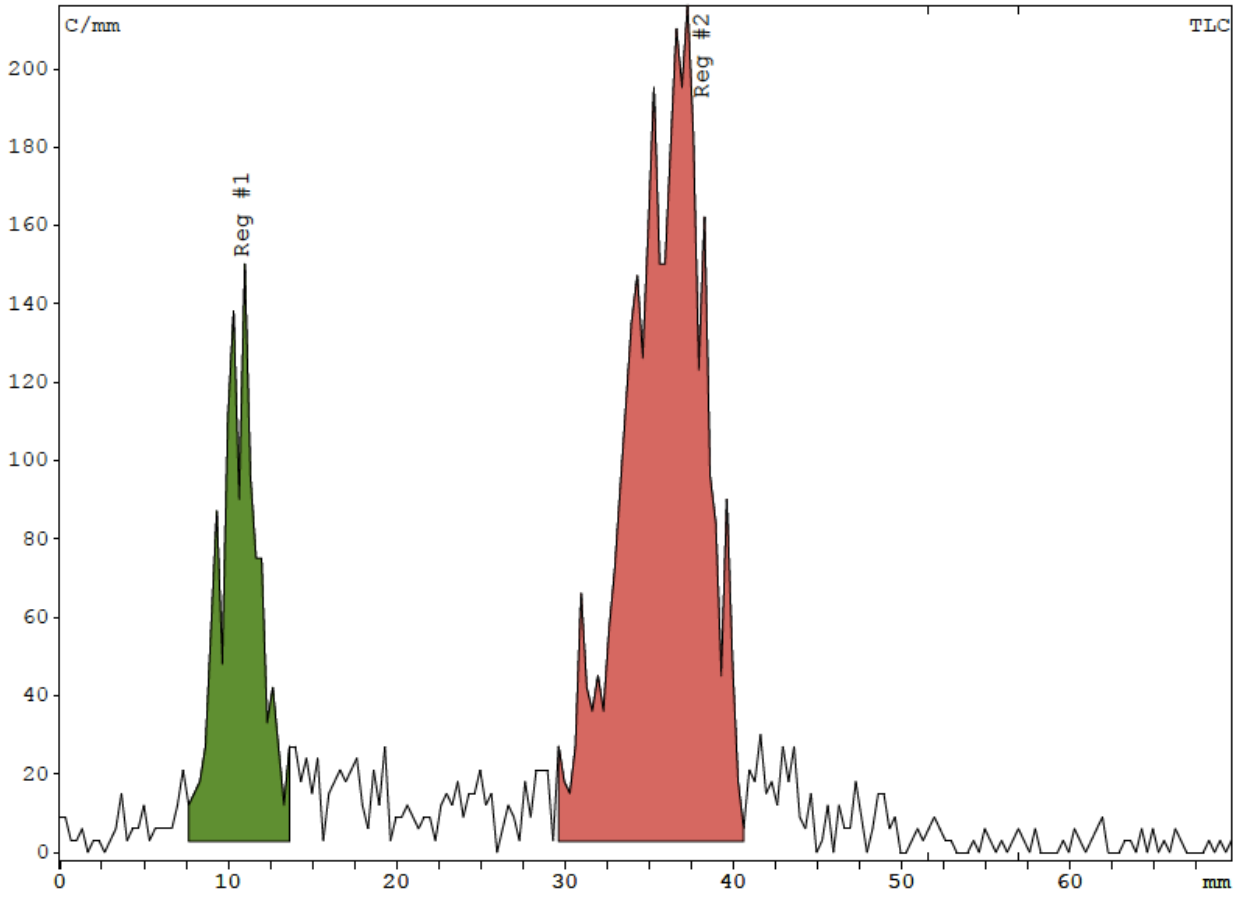
Standard procedure + 100 mol% PPh_3 + 1 min N_2 20 min:



Integration TLC

Substance	R/F	%Total	Type	Area	%Area
		%		Counts	%
Reg #1	0,181	27,51	DD	568,000	29,71
Reg #2	0,576	65,08	DD	1344,000	70,29
Sum in ROI				1912,000	
Total area				2065,000	
Area RF				2063,000	
BKG1				6,0074	

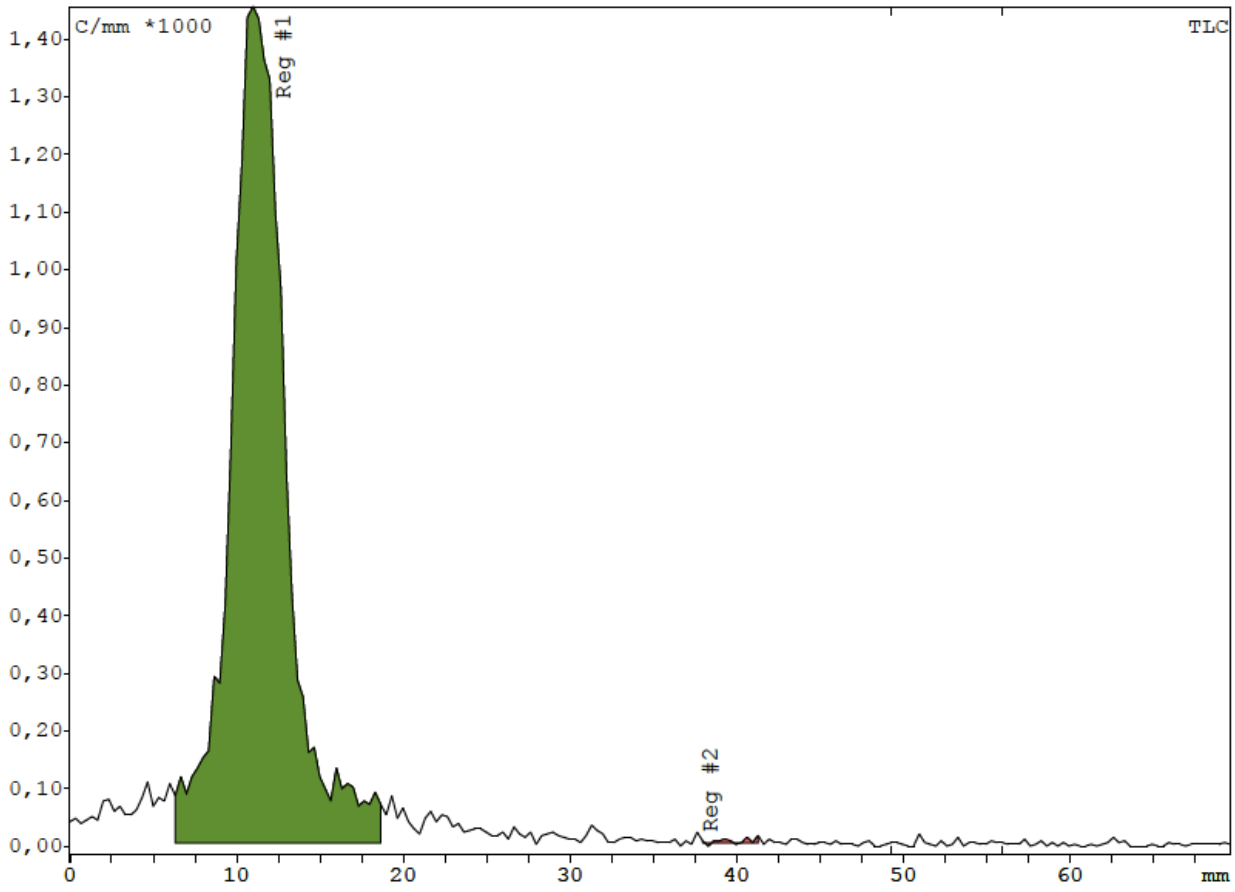
Standard procedure + 100 mol% PPh_3 + 1 min N_2 30 min:



Integration TLC

Substance	R/F	%Total	Type	Area	%Area
		%		Counts	%
Reg #1	0,152	20,52	DD	354,125	24,54
Reg #2	0,529	63,10	DD	1089,063	75,46
Sum in ROI				1443,188	
Total area				1726,063	
Area RF				1725,125	
BKG1				2,8160	

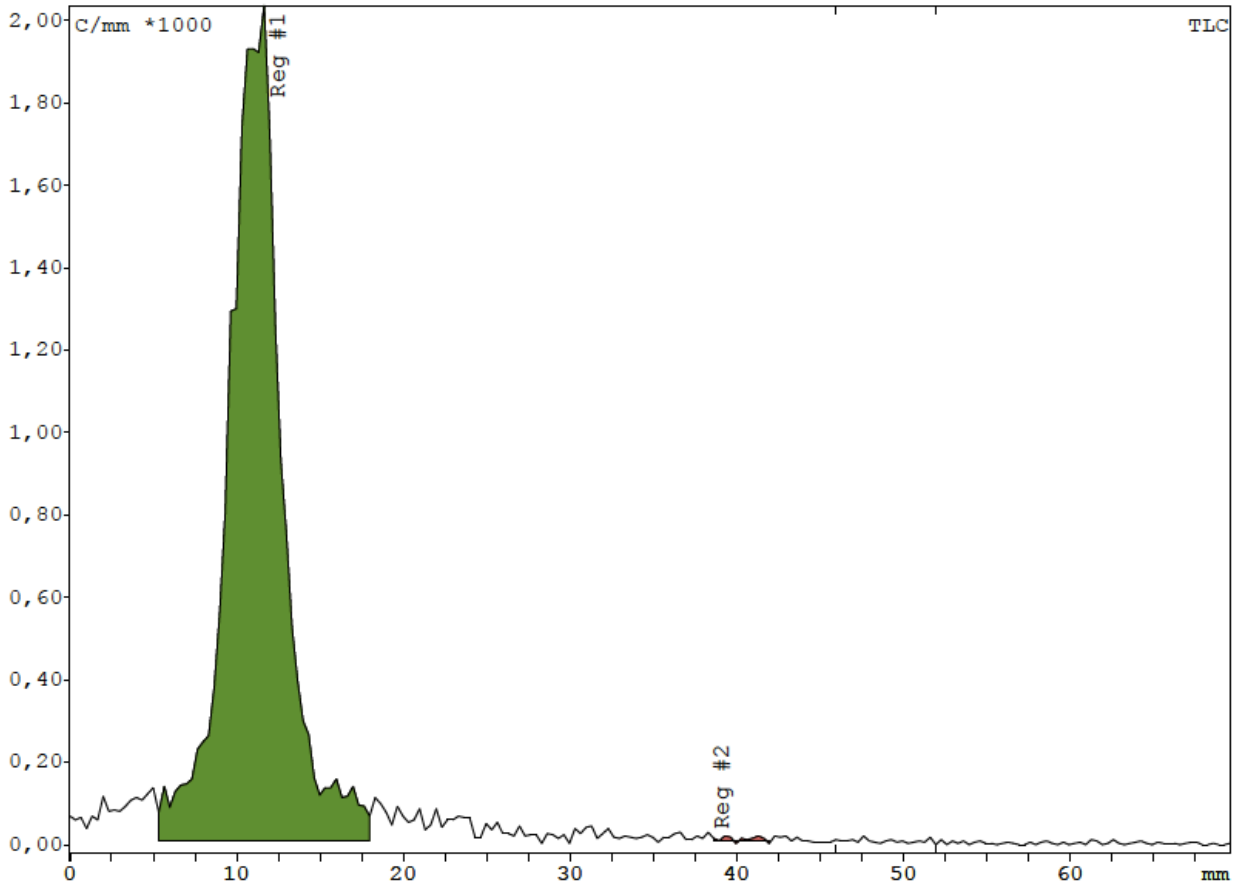
Standard procedure 0 min:



Integration TLC

Substance	R/F	%Total	Type	Area	%Area
		%		Counts	%
Reg #1	0,162	88,10	DD	5552,250	99,85
Reg #2	0,548	0,13	DD	8,500	0,15
Sum in ROI				5560,750	
Total area				6302,250	
Area RF				6302,500	
BKG1				5,2565	

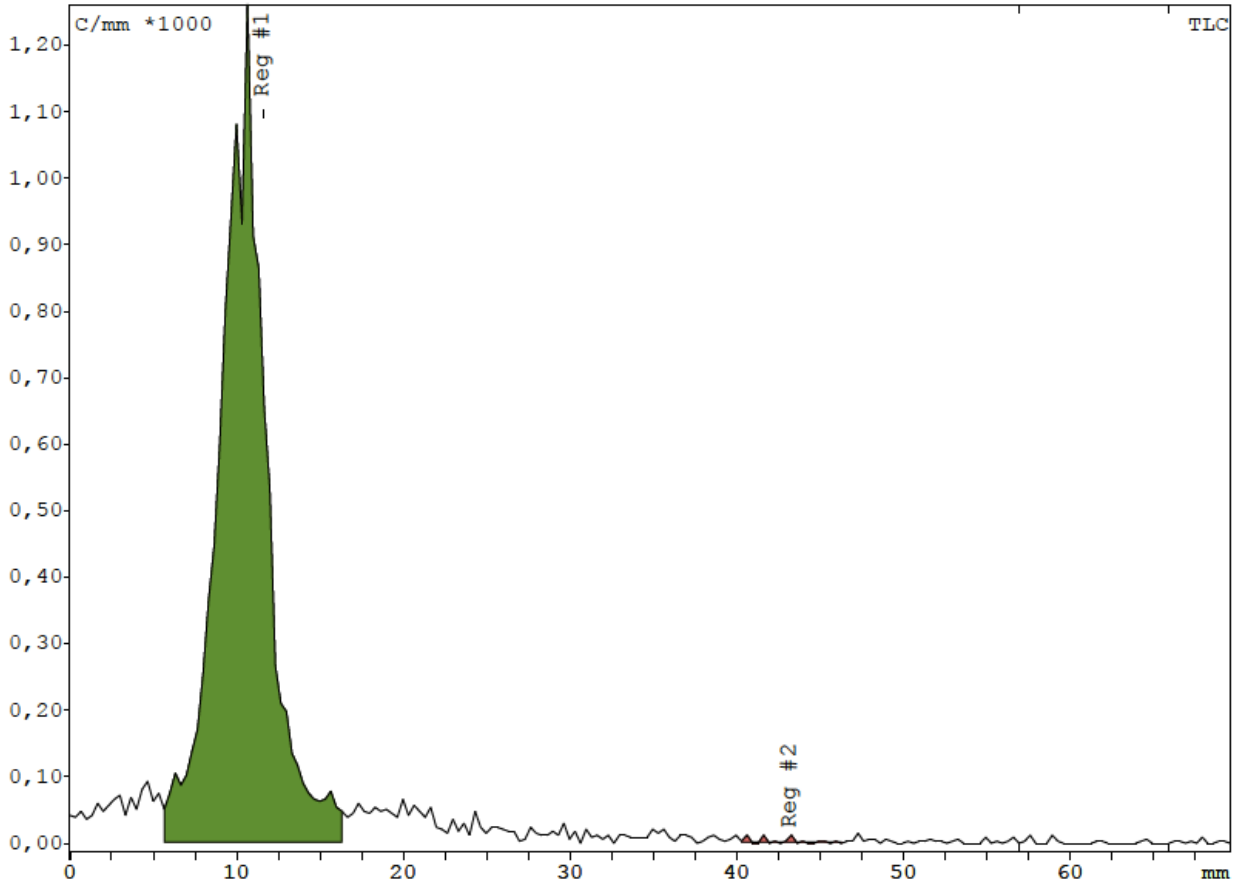
Standard procedure 1 min:



Integration TLC

Substance	R/F	%Total	Type	Area	%Area
		%		Counts	%
Reg #1	0,157	88,92	DD	7538,889	99,77
Reg #2	0,557	0,21	DD	17,444	0,23
Sum in ROI				7556,333	
Total area				8478,389	
Area RF				8475,333	
BKG1				9,1780	

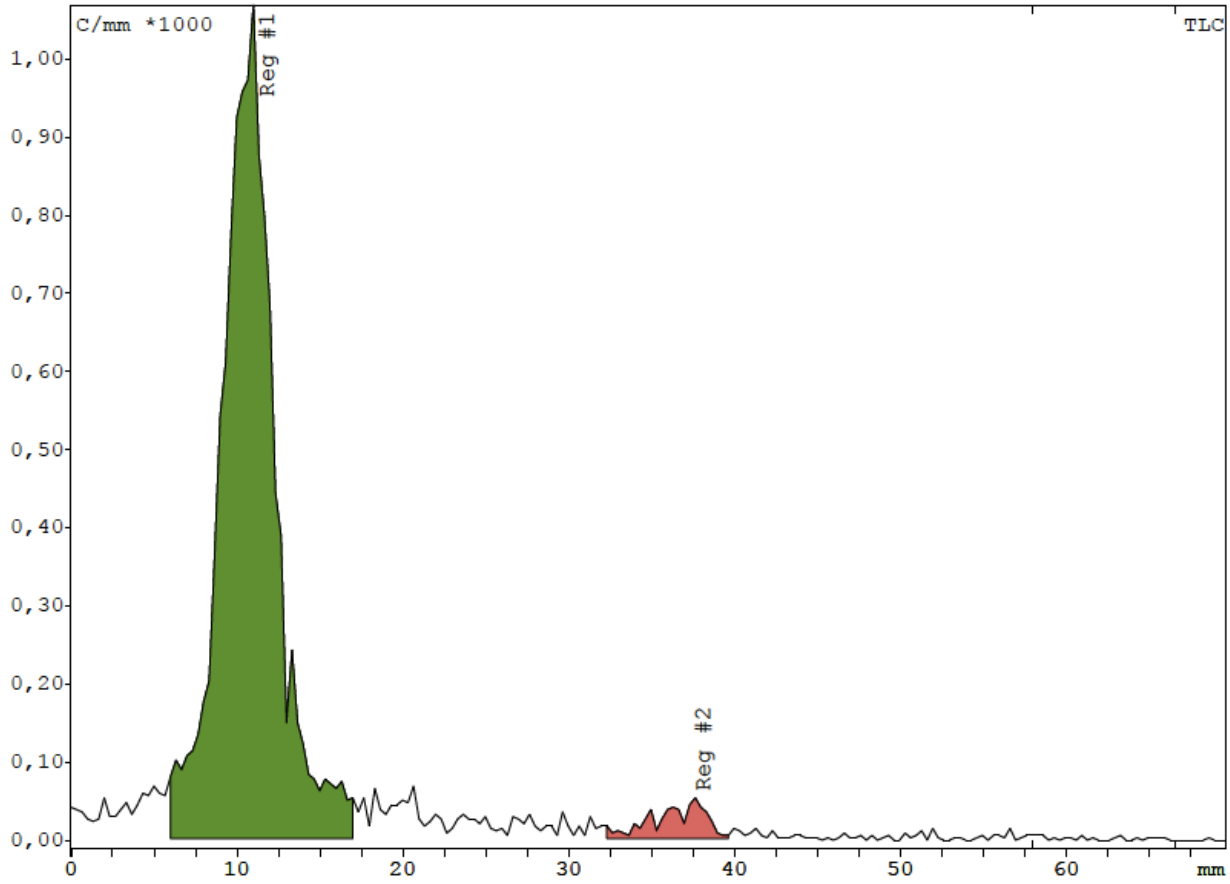
Standard procedure 2 min:



Integration TLC

Substance	R/F	%Total	Type	Area	%Area
		%		Counts	%
Reg #1	0,148	82,32	DD	3910,222	99,77
Reg #2	0,614	0,19	DD	9,000	0,23
Sum in ROI				3919,222	
Total area				4749,889	
Area RF				4750,333	
BKG1				1,6687	

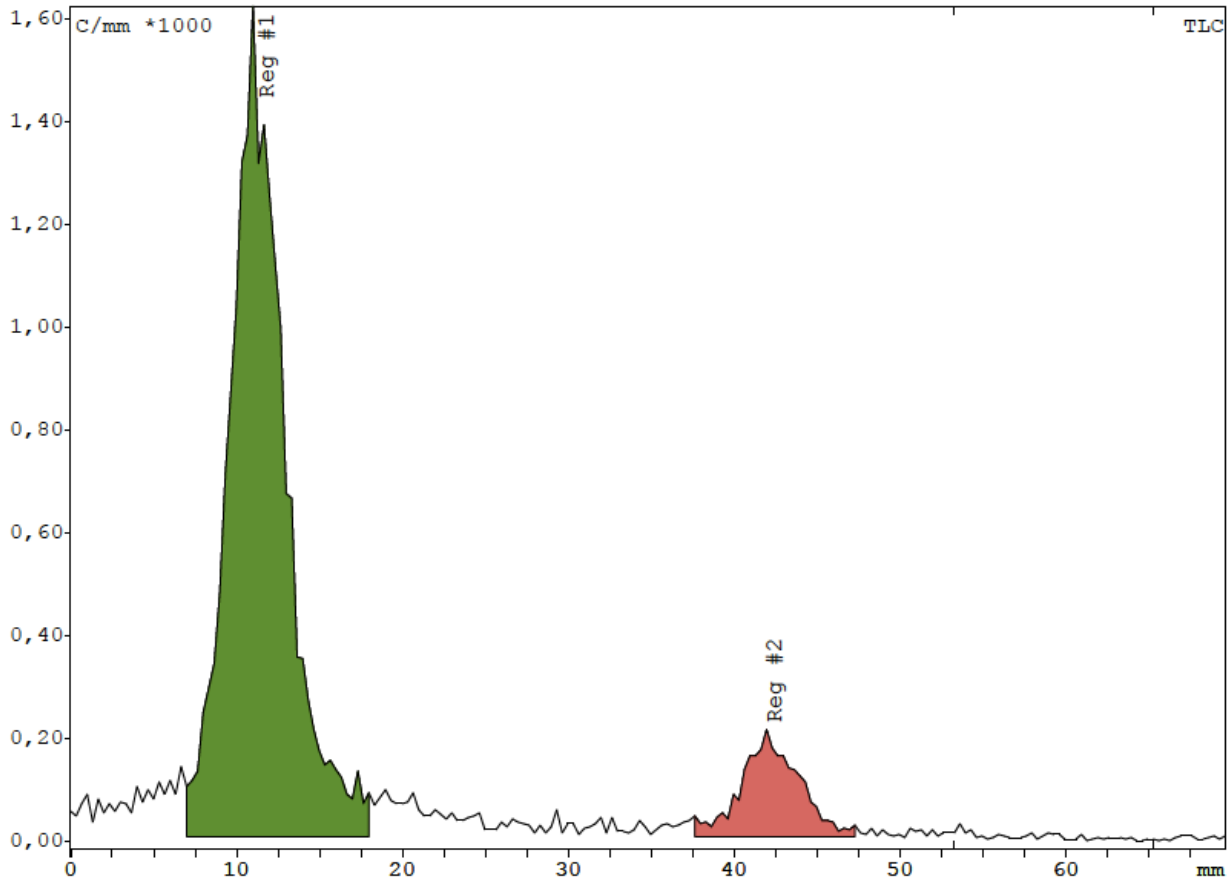
Standard procedure 3 min:



Integration TLC

Substance	R/F	%Total	Type	Area	%Area
		%		Counts	%
Reg #1	0,152	82,26	DD	3860,615	95,85
Reg #2	0,543	3,56	DD	167,077	4,15
Sum in ROI				4027,692	
Total area				4693,231	
Area RF				4692,462	
BKG1				2,3106	

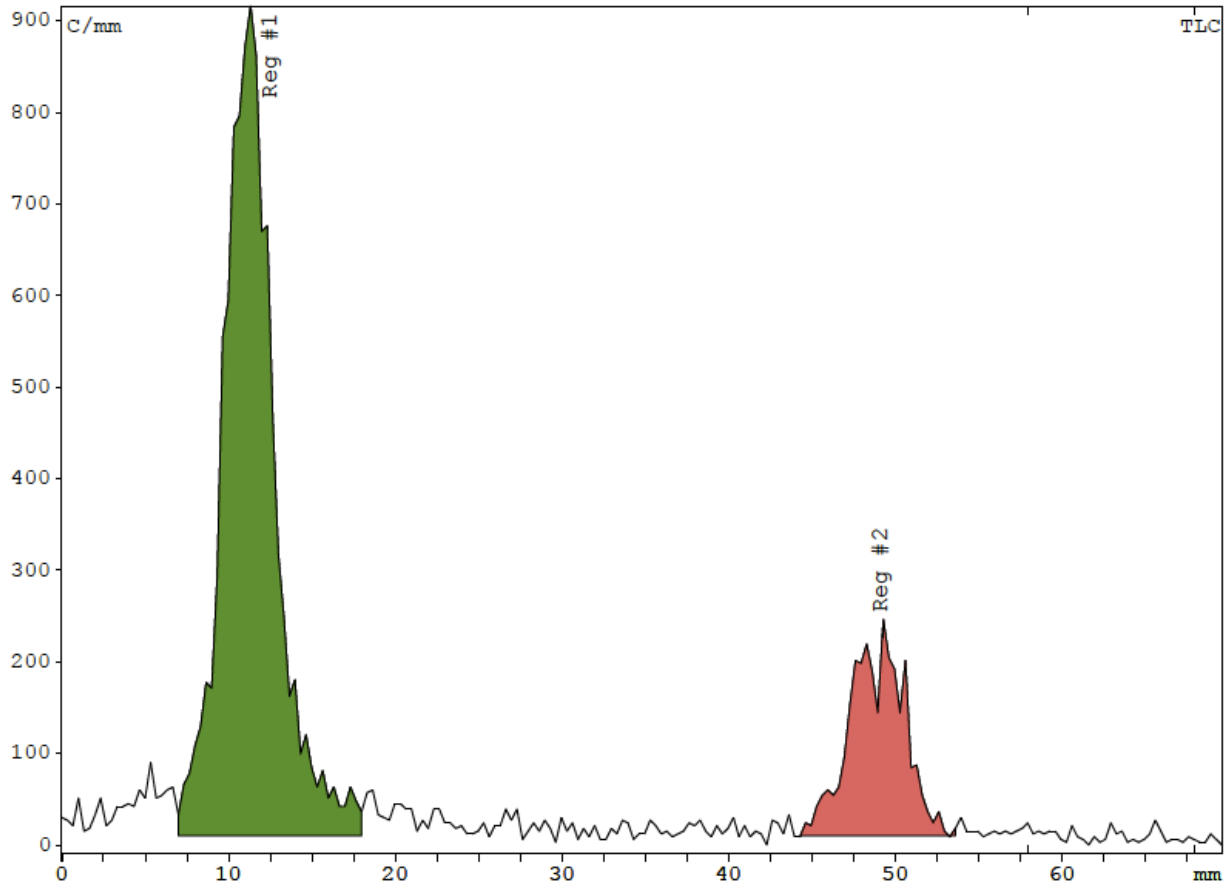
Standard procedure 4 min:



Integration TLC

Substance	R/F	%Total	Type	Area	%Area
		%		Counts	%
Reg #1	0,157	75,26	DD	6049,917	88,19
Reg #2	0,605	10,08	DD	810,472	11,81
Sum in ROI				6860,389	
Total area				8038,472	
Area RF				8036,833	
BKG1				7,9265	

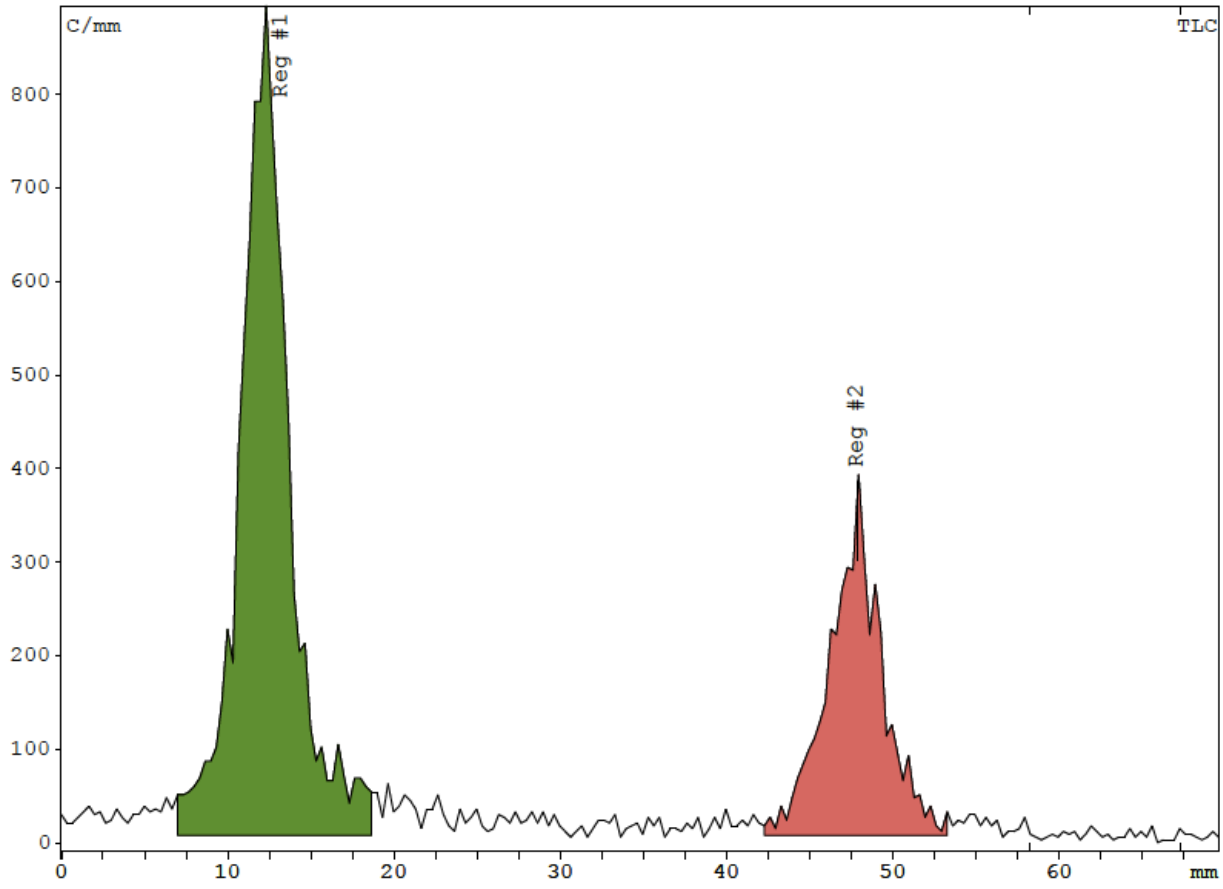
Standard procedure 5 min:



Integration TLC

Substance	R/F	%Total	Type	Area	%Area
		%		Counts	%
Reg #1	0,157	69,68	DD	3188,800	78,80
Reg #2	0,700	18,74	DD	857,800	21,20
Sum in ROI				4046,600	
Total area				4576,400	
Area RF				4575,000	
BKG1				10,2127	

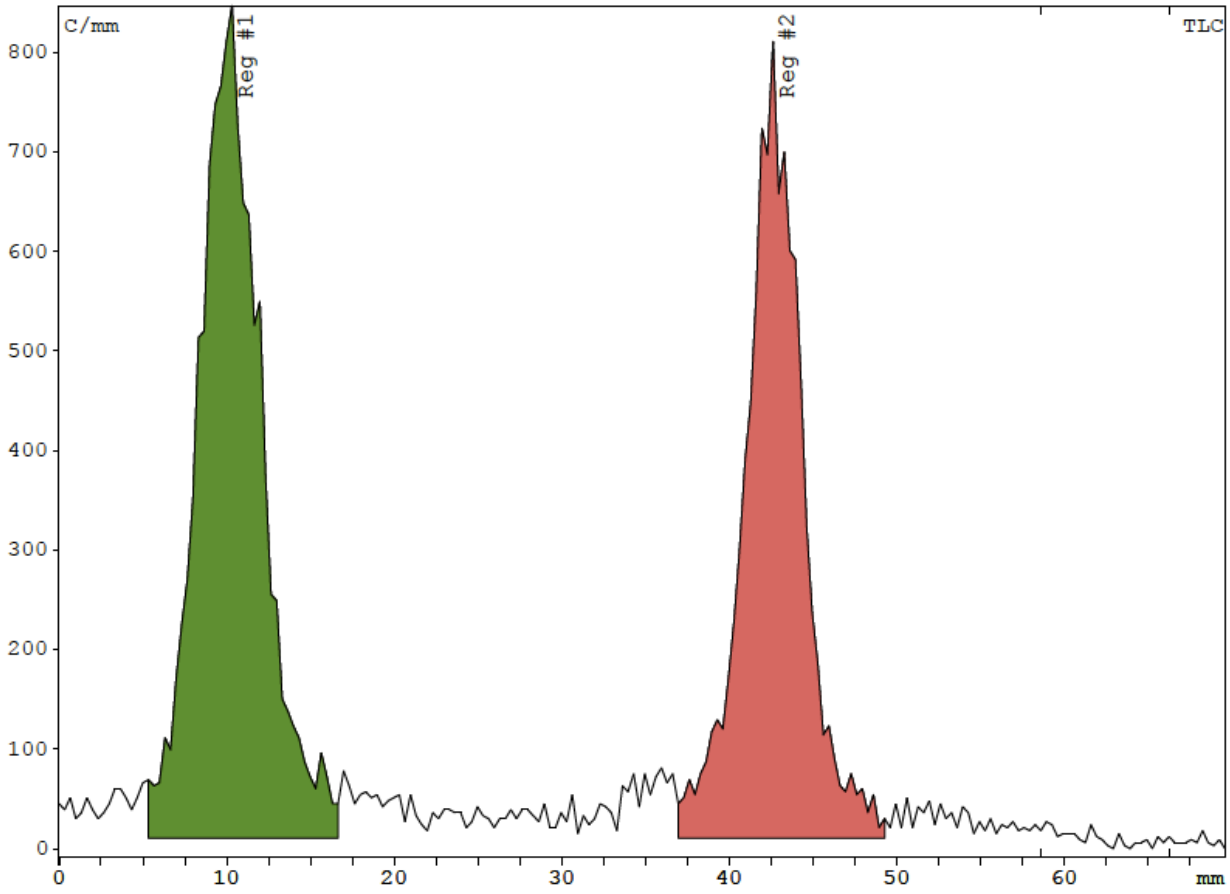
Standard procedure 6 min:



Integration TLC

Substance	R/F	%Total	Type	Area	%Area
		%		Counts	%
Reg #1	0,176	60,58	DD	2985,259	69,28
Reg #2	0,681	26,85	DD	1323,444	30,72
Sum in ROI				4308,704	
Total area				4928,148	
Area RF				4929,556	
BKG1				7,7874	

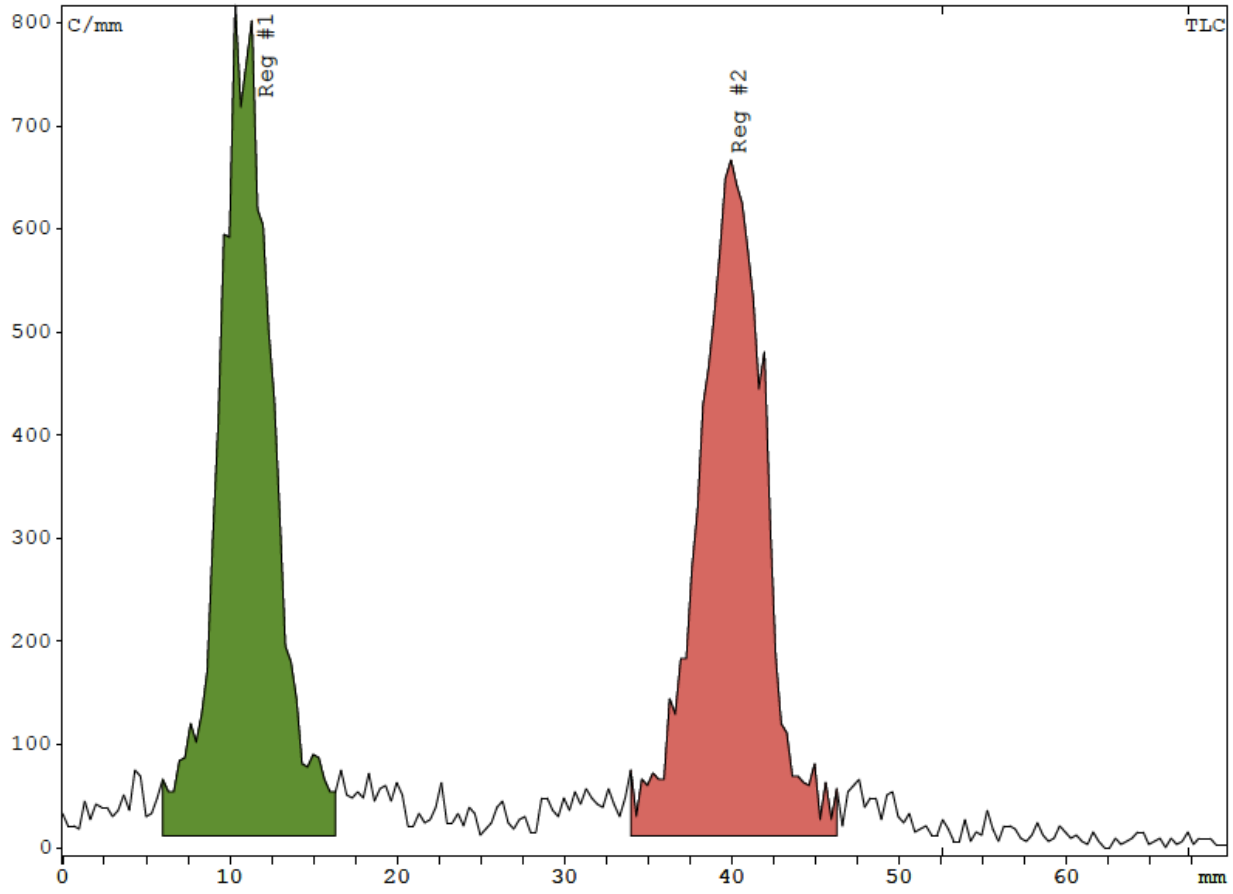
Standard procedure 8 min:



Integration TLC

Substance	R/F	%Total	Type	Area	%Area
		%		Counts	%
Reg #1	0,143	47,25	DD	3621,783	54,20
Reg #2	0,610	39,93	DD	3061,087	45,80
Sum in ROI				6682,870	
Total area				7665,870	
Area RF				7665,304	
BKG1				10,7089	

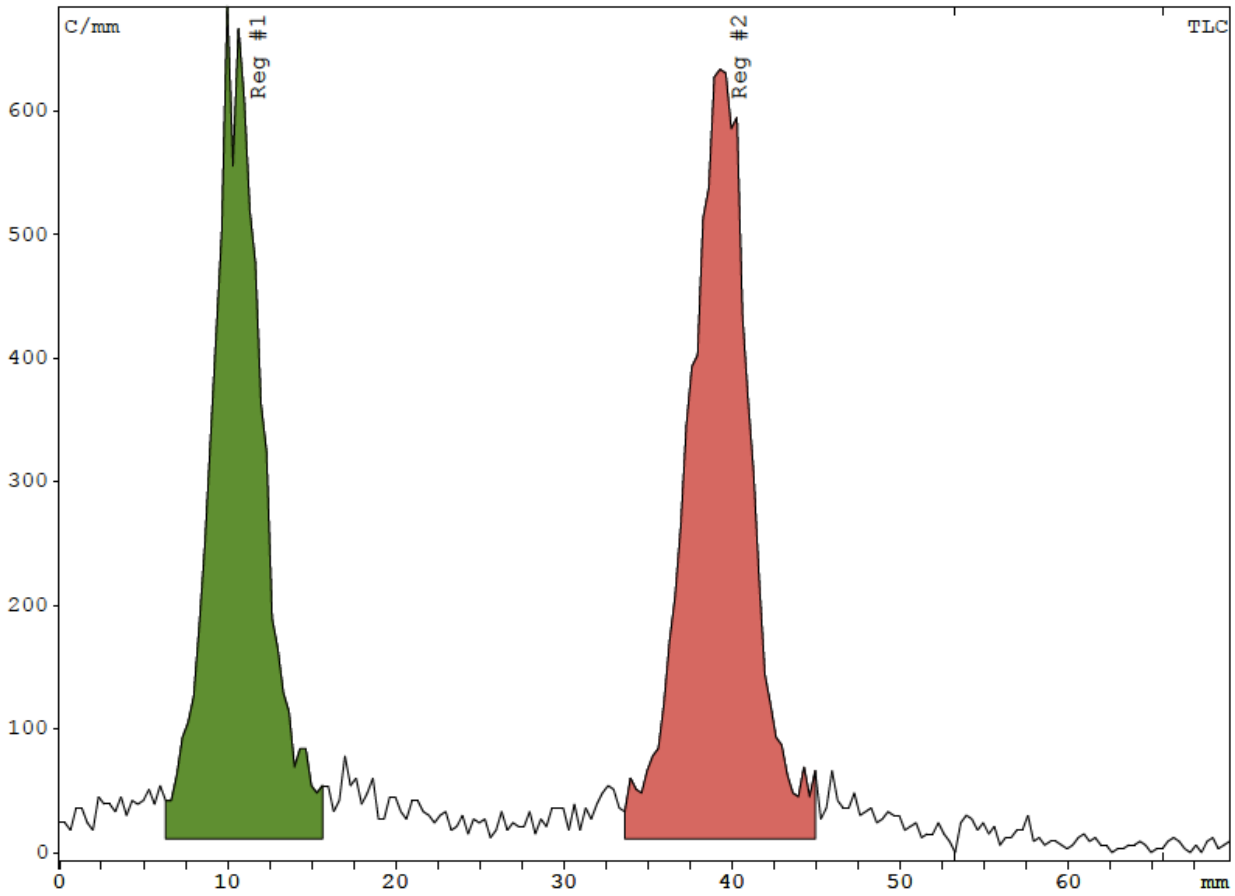
Standard procedure 10 min:



Integration TLC

Substance	R/F	%Total	Type	Area	%Area
		%		Counts	%
Reg #1	0,157	43,83	DD	2987,750	49,76
Reg #2	0,576	44,24	DD	3016,250	50,24
Sum in ROI				6004,000	
Total area				6817,250	
Area RF				6814,500	
BKG1				11,2640	

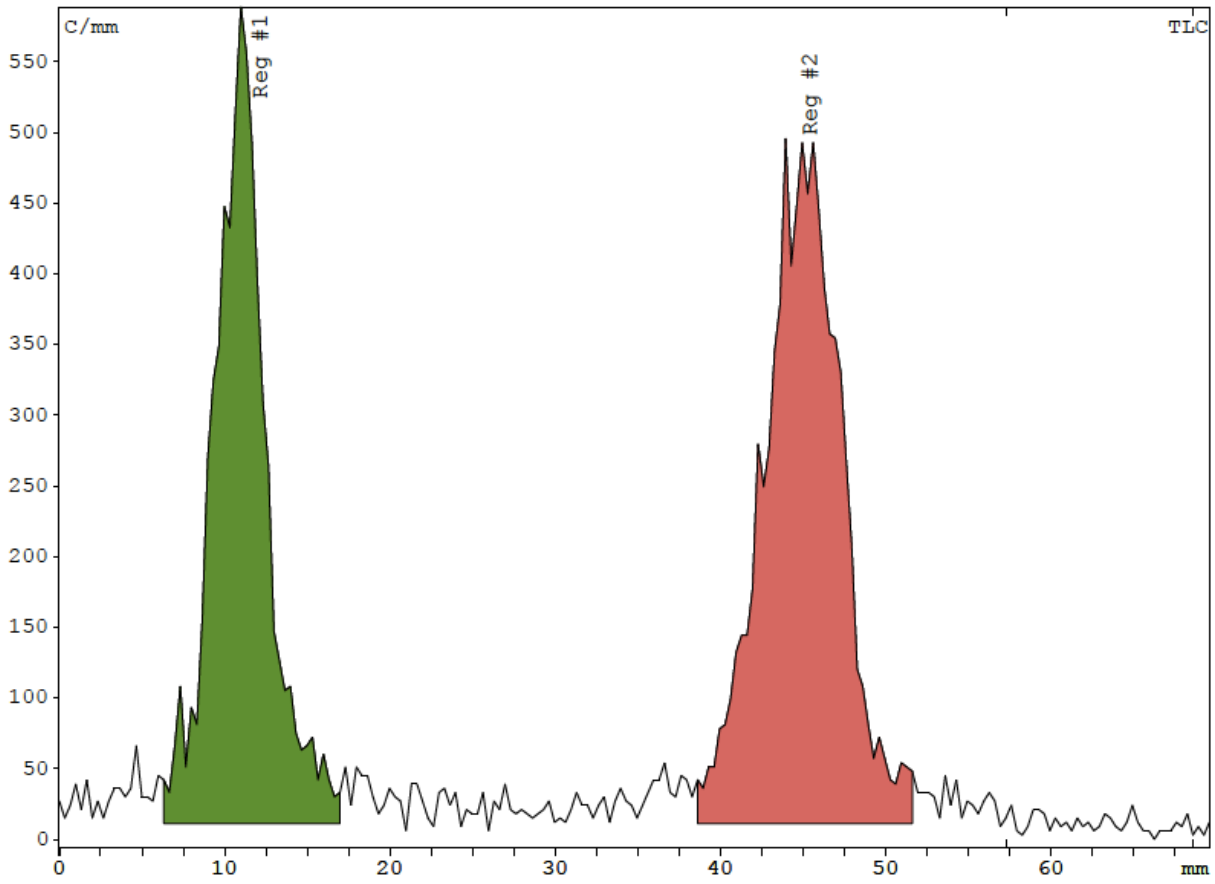
Standard procedure 12 min:



Integration TLC

Substance	R/F	%Total	Type	Area	%Area
		%		Counts	%
Reg #1	0,152	40,56	DD	2325,324	46,26
Reg #2	0,567	47,11	DD	2701,108	53,74
Sum in ROI				5026,432	
Total area				5733,135	
Area RF				5731,432	
BKG1				11,1219	

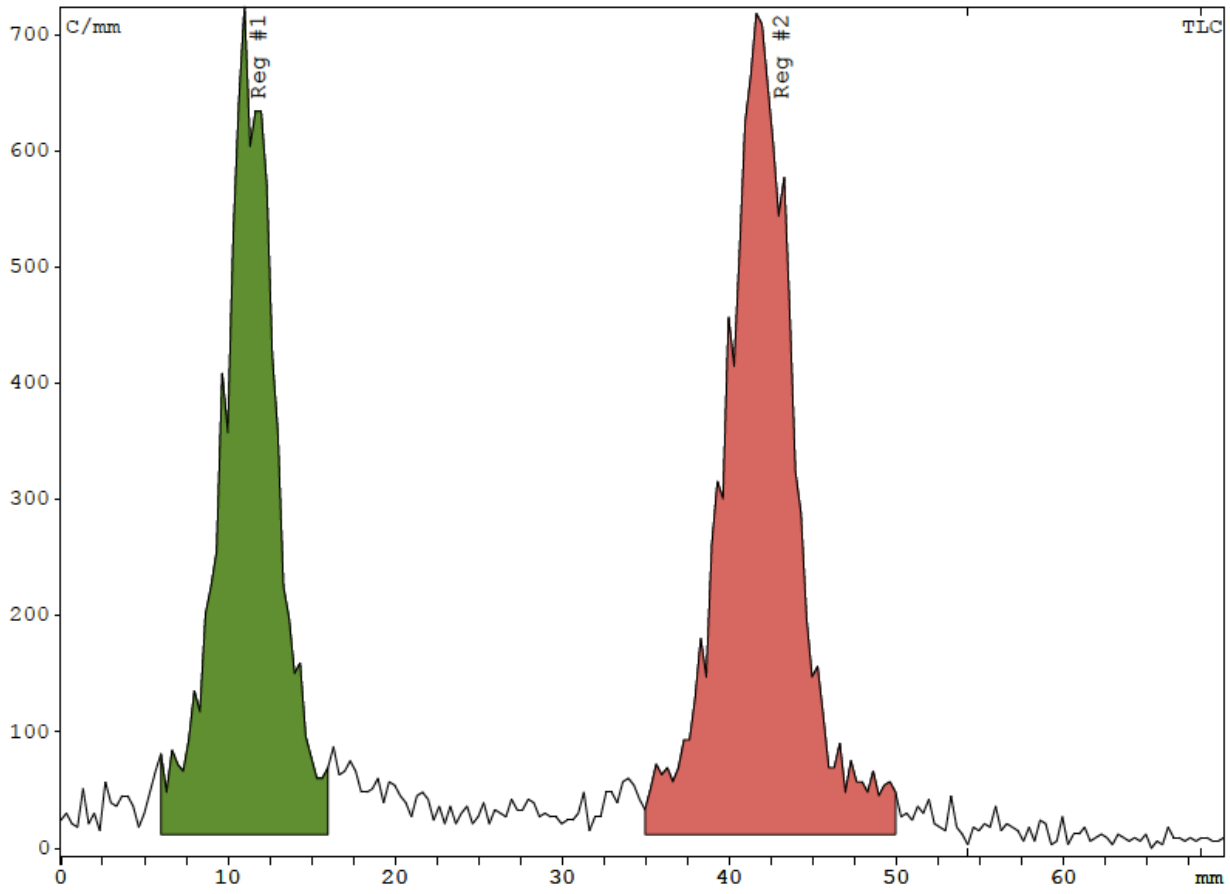
Procedure **15** **min:**



Integration TLC

Substance	R/F	%Total	Type	Area	%Area
		%		Counts	%
Reg #1	0,157	38,98	DD	2047,471	43,61
Reg #2	0,648	50,40	DD	2647,324	56,39
Sum in ROI				4694,794	
Total area				5252,324	
Area RF				5249,588	
BKG1				11,2198	

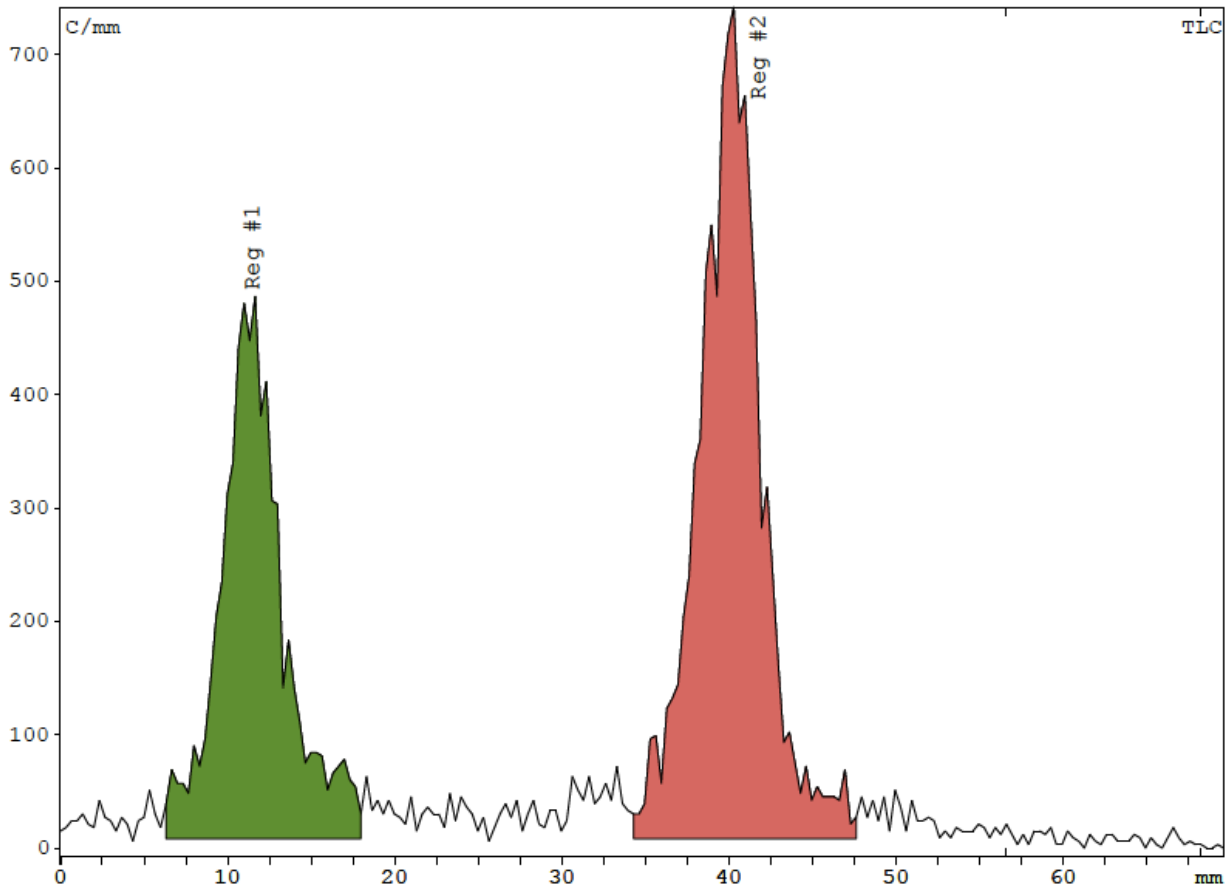
Standard procedure 20 min:



Integration TLC

Substance	R/F	%Total	Type	Area	%Area
		%		Counts	%
Reg #1	0,162	38,74	DD	2642,143	43,49
Reg #2	0,595	50,33	DD	3433,214	56,51
Sum in ROI				6075,357	
Total area				6820,929	
Area RF				6819,000	
BKG1				11,8003	

Standard procedure 30 min:

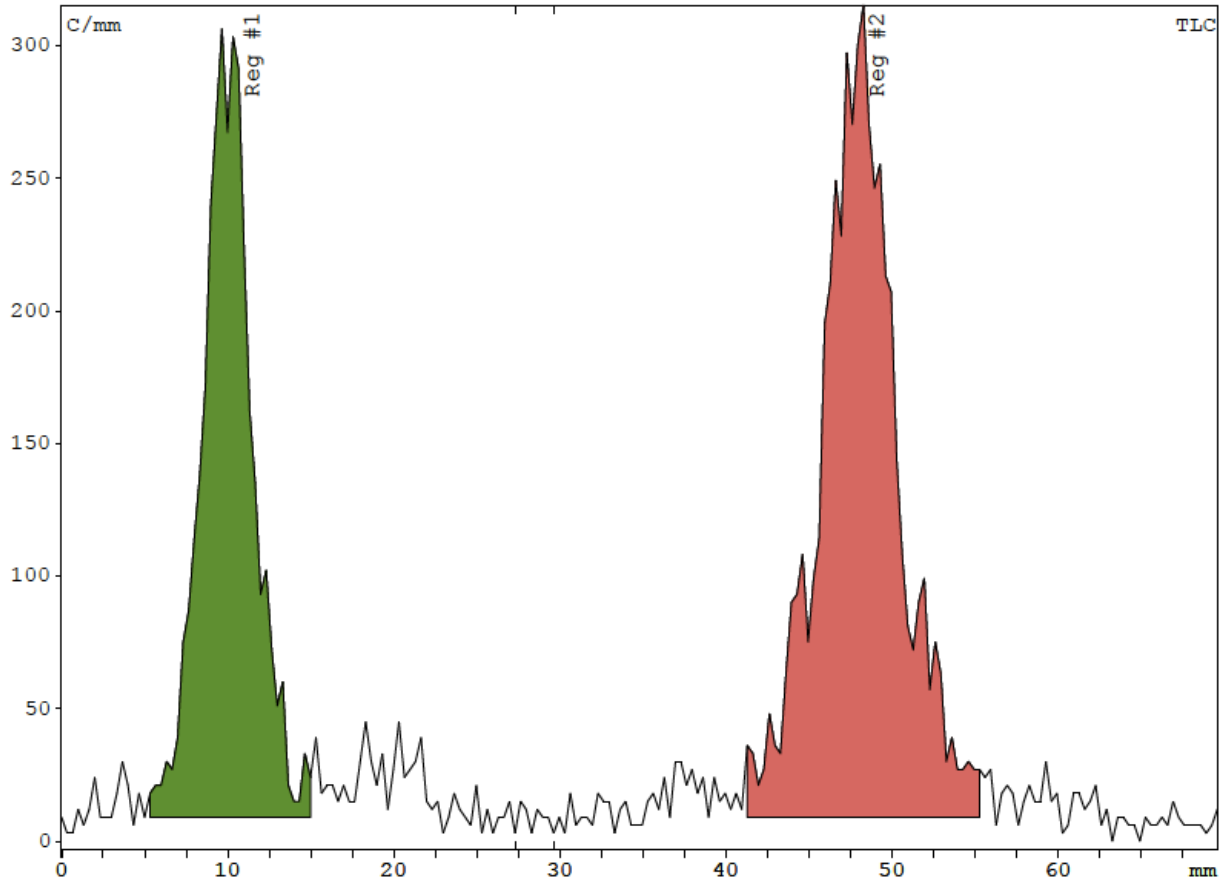


Integration TLC

Substance	R/F	%Total	Type	Area	%Area
		%		Counts	%
Reg #1	0,162	34,74	DD	2003,000	39,21
Reg #2	0,576	53,85	DD	3105,143	60,79
Sum in ROI				5108,143	
Total area				5765,771	
Area RF				5764,000	
BKG1				8,3246	

11.3 RadioTLC carrier added experiments

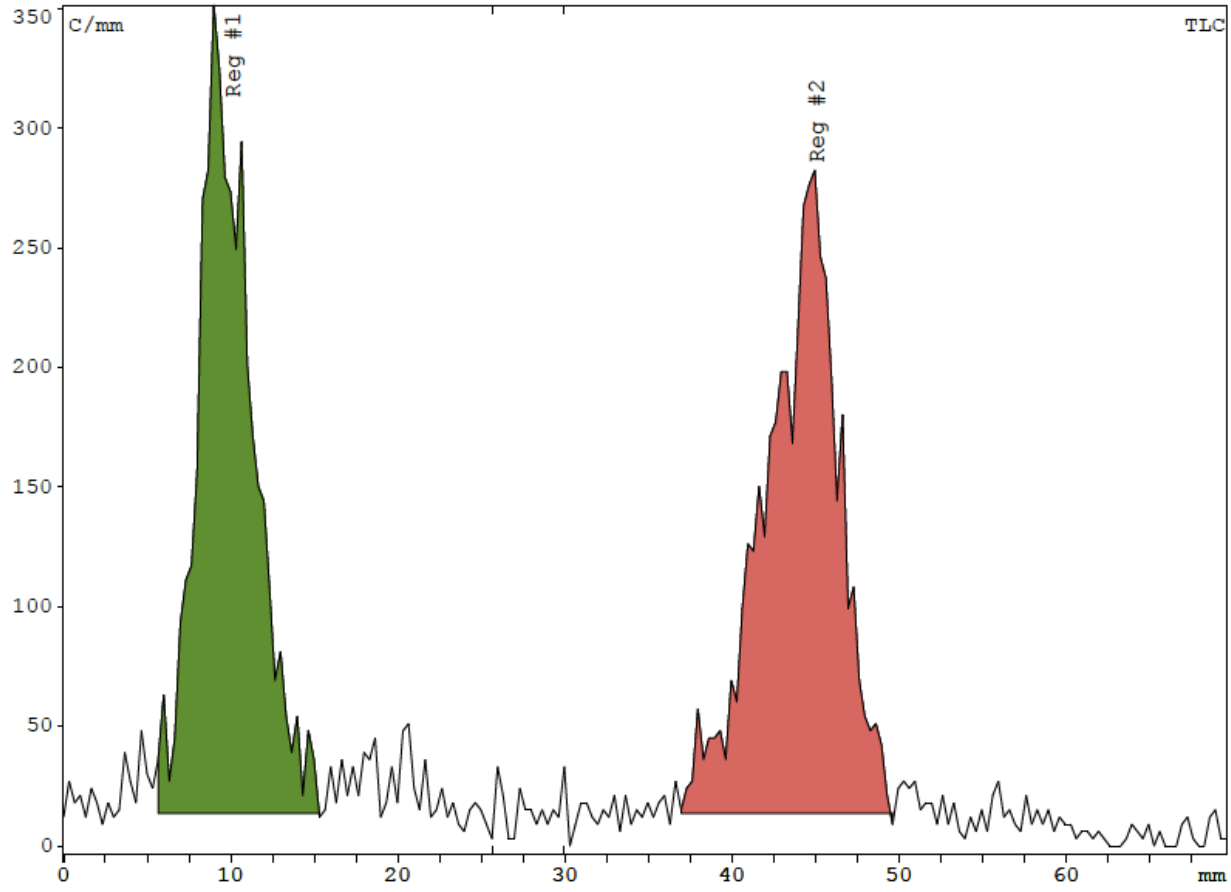
Standard conditions +0.00001 equivalents (KF:K222:K_2CO_3; 1:4:1); 100mol% PPh_3



Integration TLC

Substance	R/F	%Total	Type	Area	%Area
		%		Counts	%
Reg #1	0,143	36,48	DD	1047,000	39,95
Reg #2	0,686	54,84	DD	1574,000	60,05
Sum in ROI				2621,000	
Total area				2870,000	
Area RF				2869,000	
BKG1				9,0112	

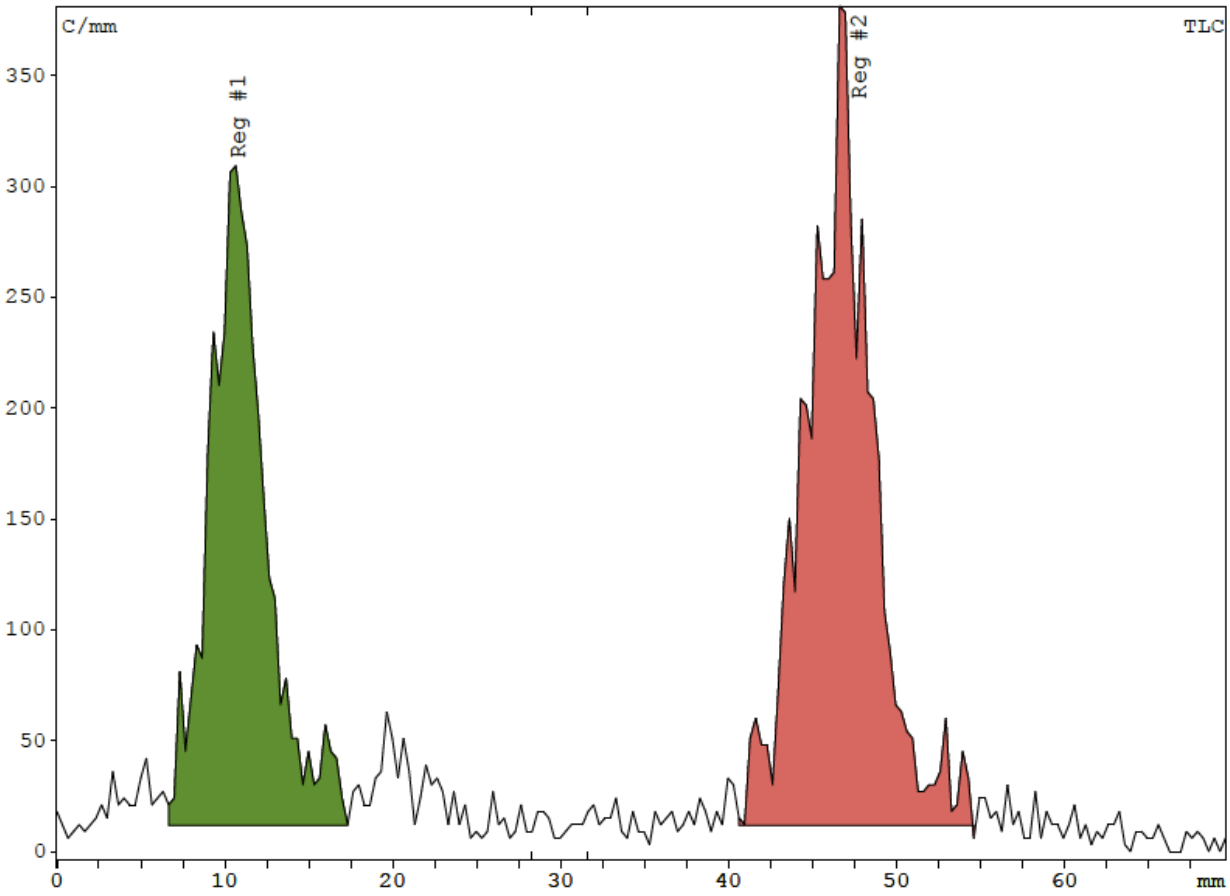
Standard conditions +0.0001 equivalents (KF:K222:K_2CO_3; 1:4:1); 100mol% PPh_3



Integration TLC

Substance	R/F	%Total	Type	Area	%Area
		%		Counts	%
Reg #1	0,133	46,91	DD	1250,385	48,28
Reg #2	0,643	50,26	DD	1339,538	51,72
Sum in ROI				2589,923	
Total area				2665,462	
Area RF				2661,923	
BKG1				13,6323	

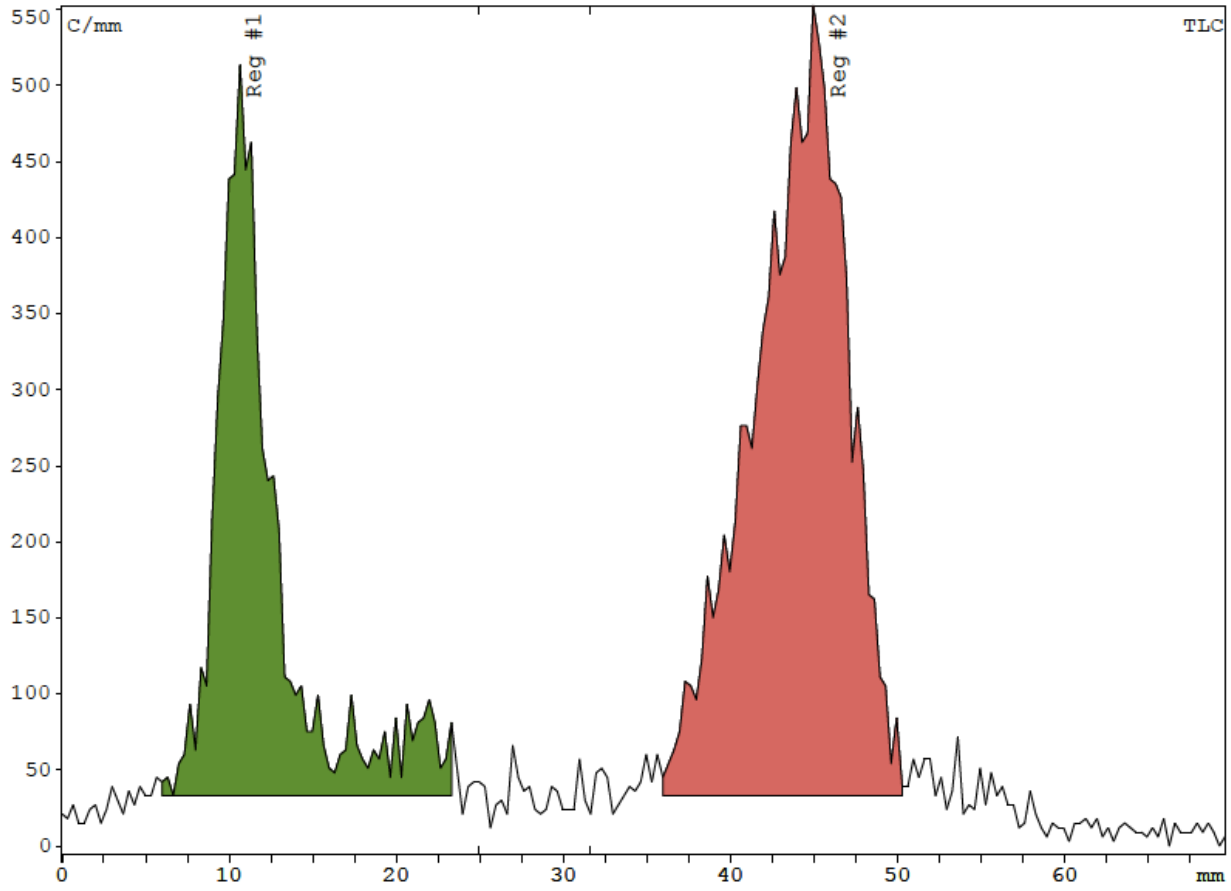
Standard conditions +0.0001 equivalents (KF:K222:K_2CO_3; 1:4:1); 100mol% PPh_3



Integration TLC

Substance	R/F	%Total	Type	Area	%Area
		%		Counts	%
Reg #1	0,152	39,20	DD	1151,200	41,96
Reg #2	0,667	54,21	DD	1592,200	58,04
Sum in ROI				2743,400	
Total area				2936,900	
Area RF				2933,000	
BKG1				11,7145	

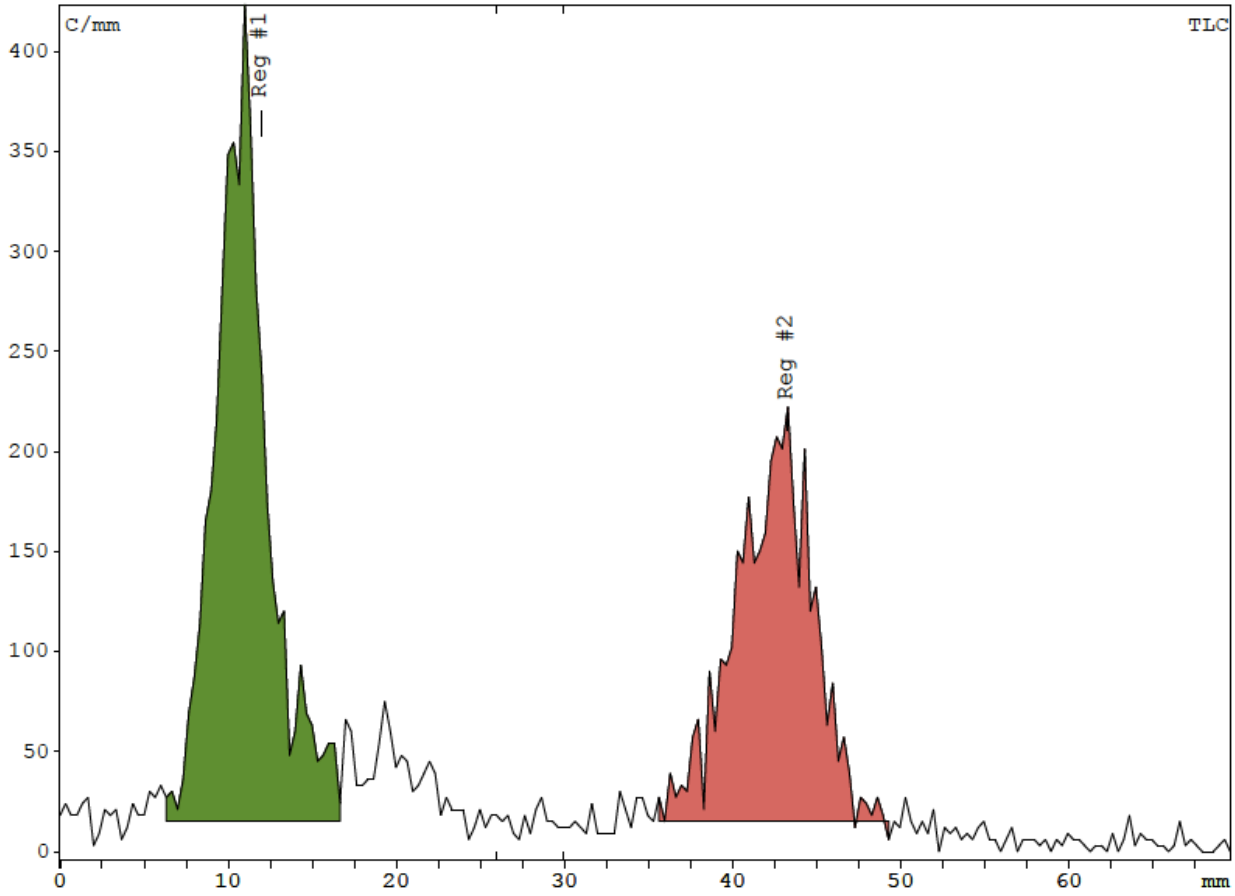
Standard conditions +0.001 equivalents (KF:K222:K_2CO_3; 1:4:1); 100mol% PPh_3



Integration TLC

Substance	R/F	%Total	Type	Area	%Area
		%		Counts	%
Reg #1	0,152	37,27	DD	1851,000	35,84
Reg #2	0,643	66,72	DD	3314,000	64,16
Sum in ROI				5165,000	
Total area				4967,000	
Area RF				4956,000	
BKG1				33,0410	

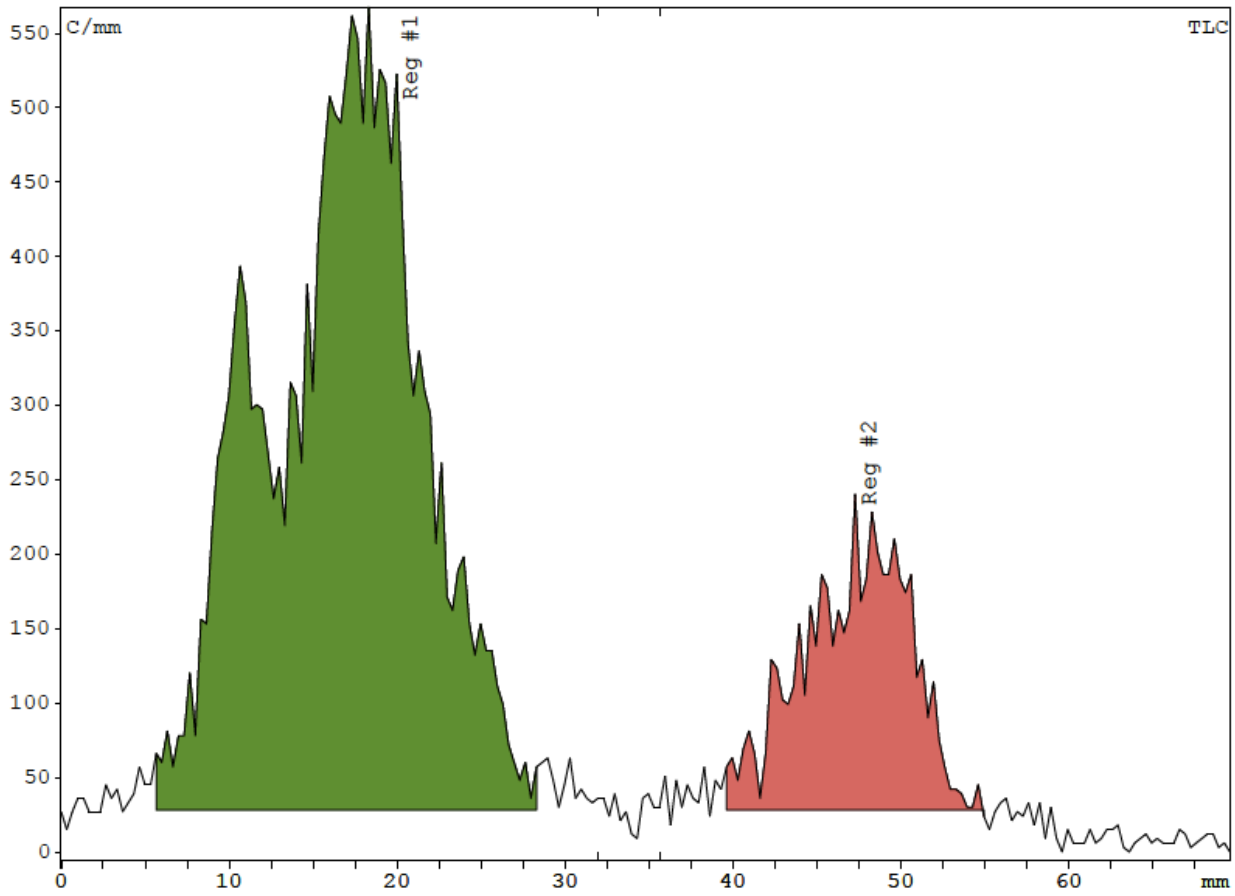
Standard conditions +0.01 equivalents (KF:K222:K_2CO_3; 1:4:1); 100mol% PPh_3



Integration TLC

Substance	R/F	%Total	Type	Area	%Area
		%		Counts	%
Reg #1	0,152	56,07	DD	1391,417	56,96
Reg #2	0,614	42,38	DD	1051,583	43,04
Sum in ROI				2443,000	
Total area				2481,583	
Area RF				2478,500	
BKG1				15,2689	

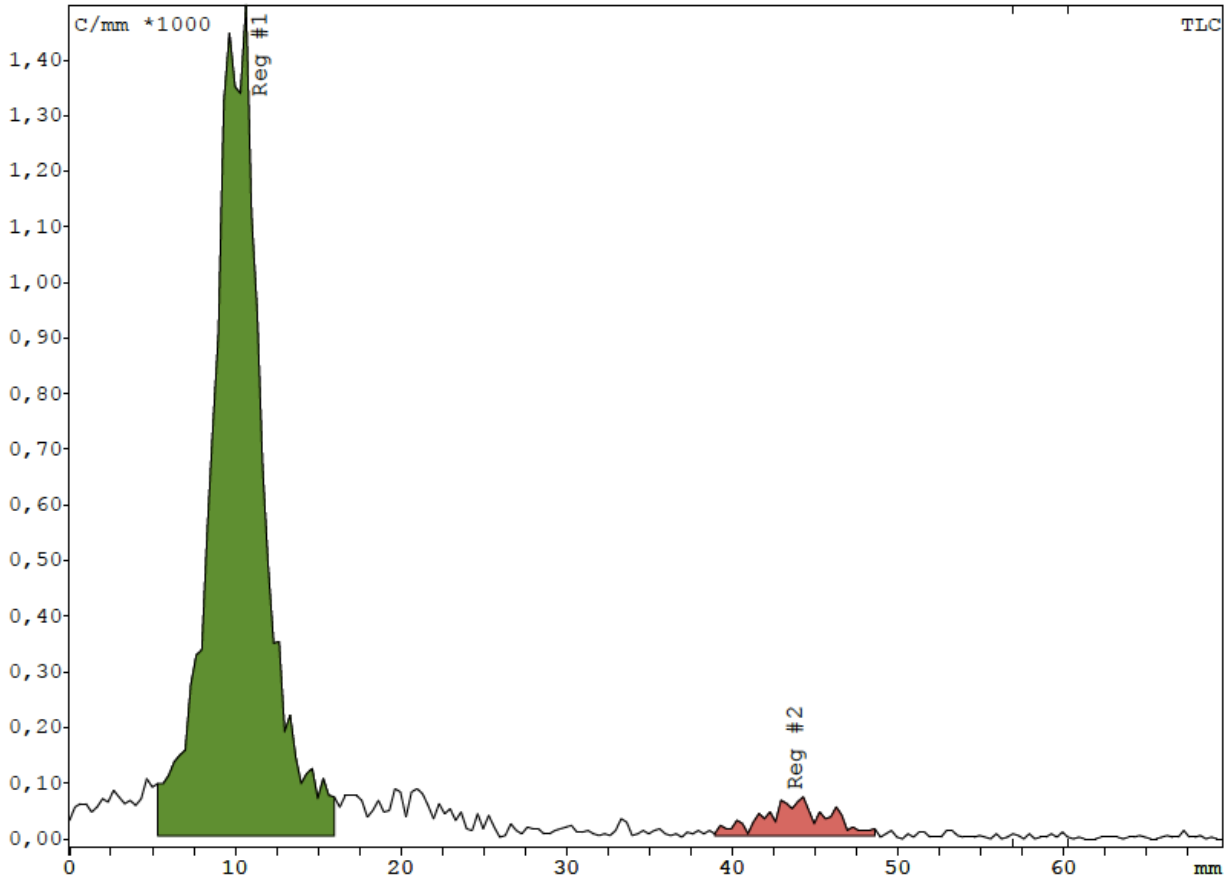
Standard conditions +0.1 equivalents (KF:K222:K_2CO_3; 1:4:1); 100mol% PPh_3



Integration TLC

Substance	R/F	%Total	Type	Area	%Area
		%		Counts	%
Reg #1	0,252	80,42	DD	5536,273	79,64
Reg #2	0,686	20,56	DD	1415,273	20,36
Sum in ROI				6951,545	
Total area				6884,000	
Area RF				6876,636	
BKG1				28,1258	

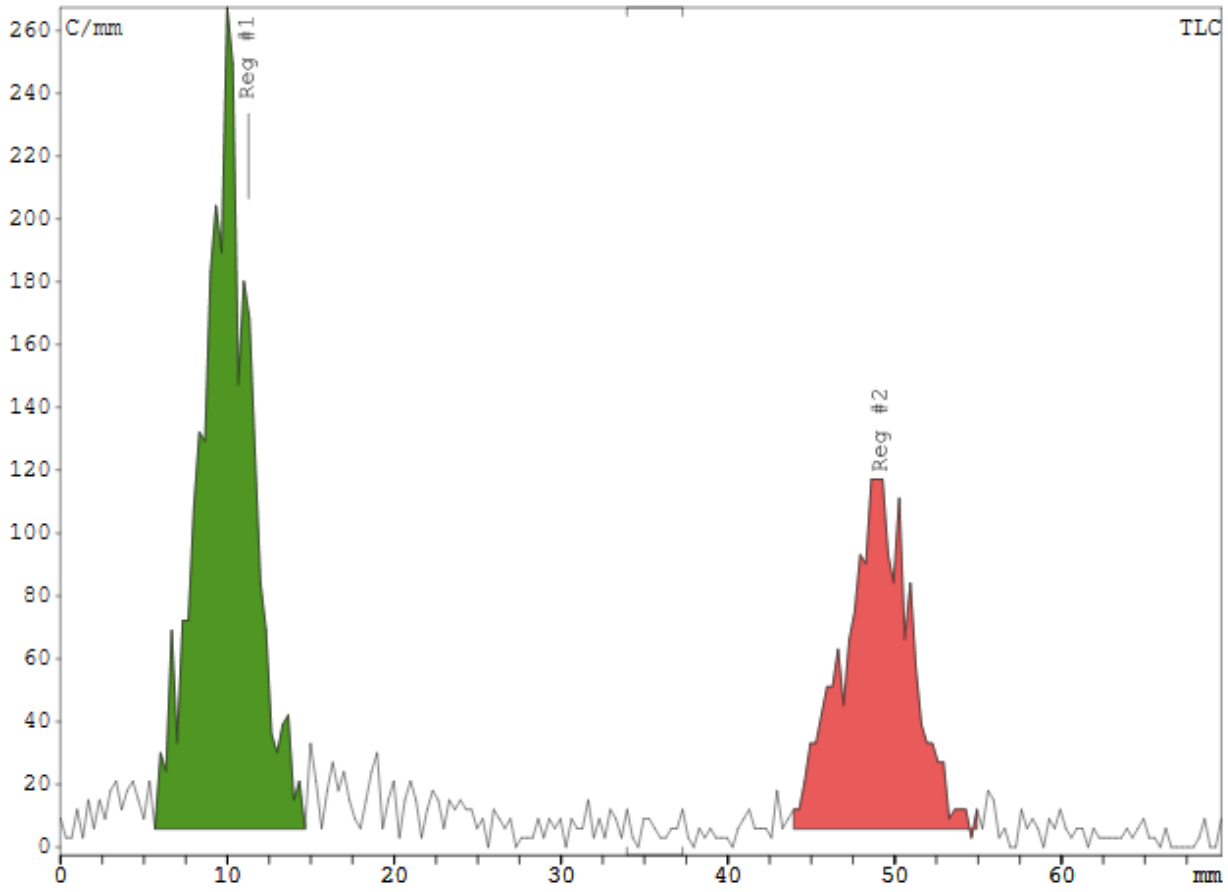
Standard conditions +1 equivalents (KF:K222:K_2CO_3; 1:4:1); 100mol% PPh_3



Integration TLC

Substance	R/F	%Total	Type	Area	%Area
		%		Counts	%
Reg #1	0,143	81,27	DD	5259,400	94,73
Reg #2	0,624	4,52	DD	292,800	5,27
Sum in ROI				5552,200	
Total area				6471,800	
Area RF				6470,000	
BKG1				5,4067	

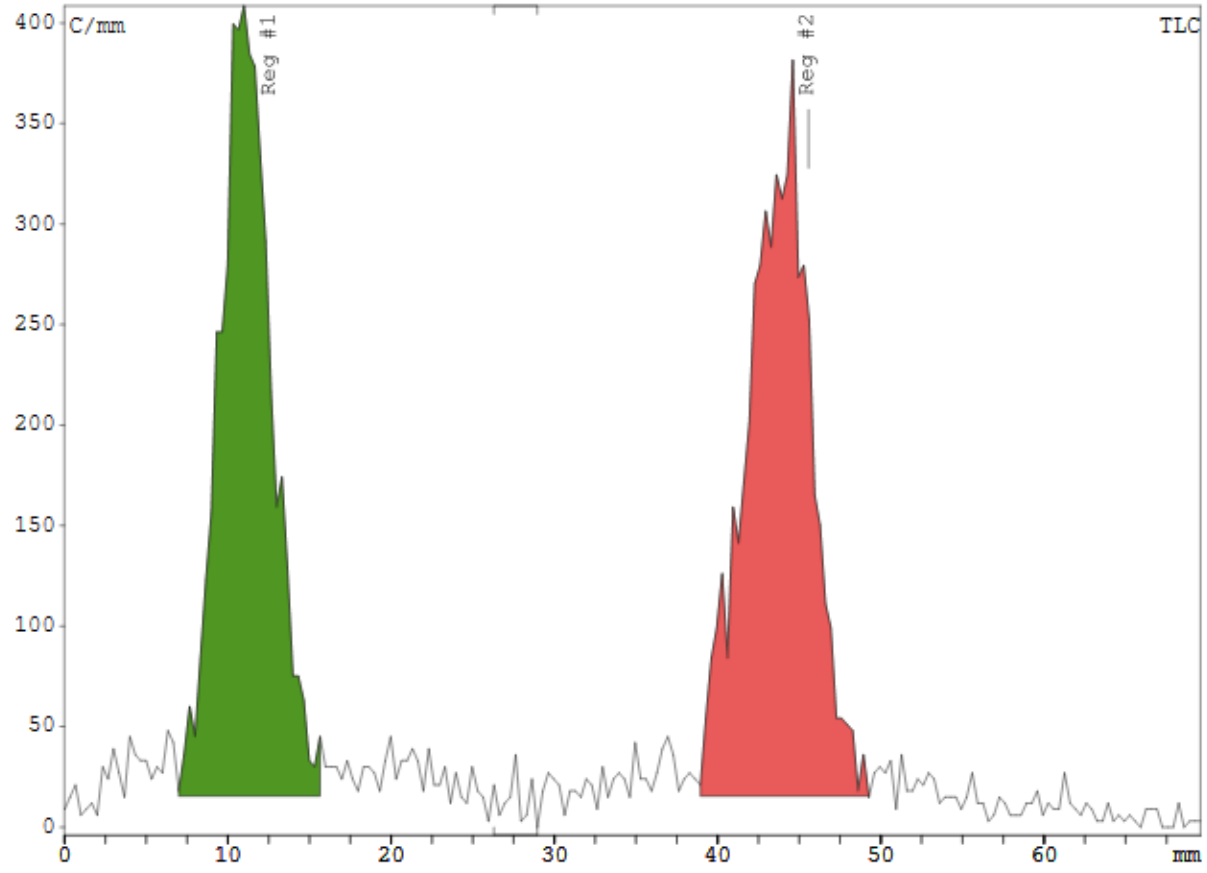
Standard conditions + 0.000001 equivalents (KF:K222:K_2CO_3; 1:4:1)



Integration TLC

Substance	R/F	%Total	Type	Area	%Area
		%		Counts	%
Reg #1	0,138	57,00	DD	856,7000	62,35
Reg #2	0,700	34,42	DD	517,3000	37,65
Sum in ROI				1374,0000	
Total area				1502,9000	
Area RF				1501,0000	
BKG1				5,70708	
Remainder RF				127,00	8,46
Remainder (Tot)				128,90	8,58

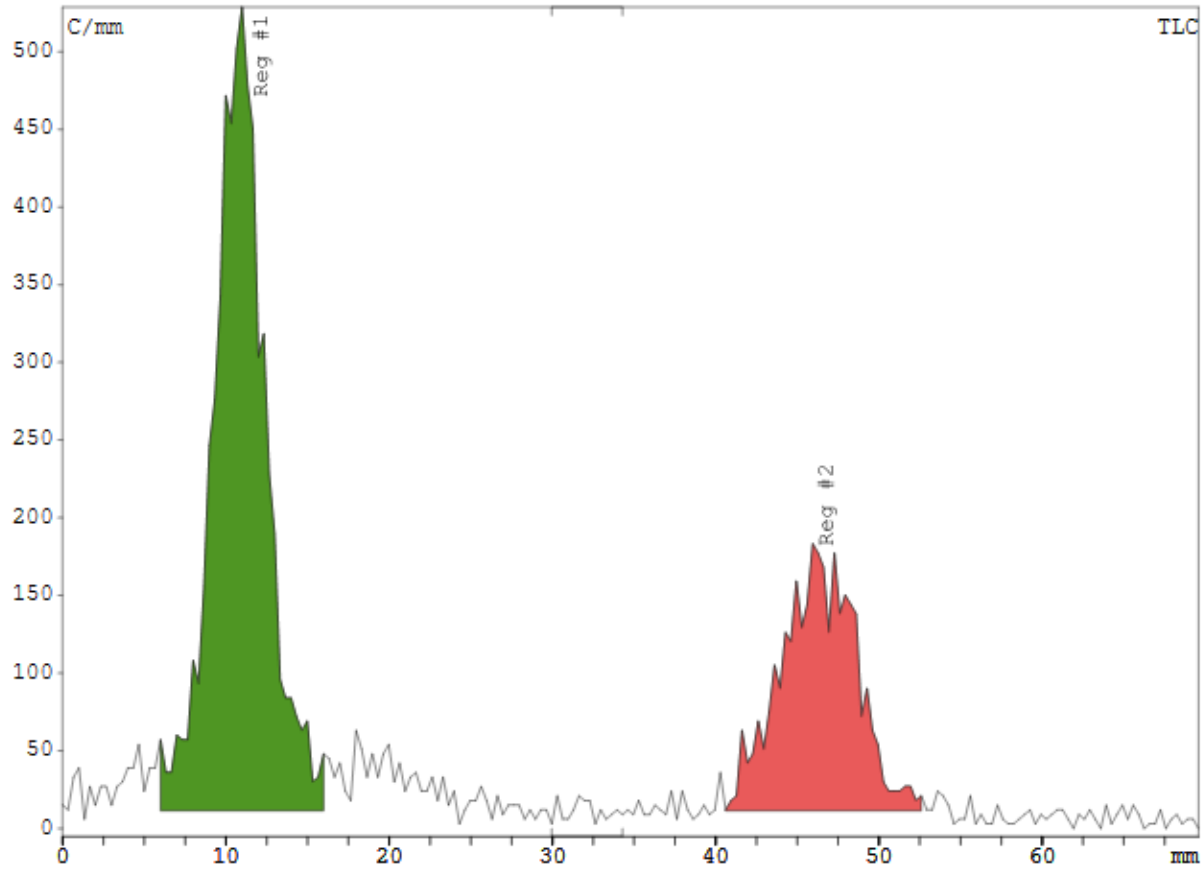
Standard conditions + 0.00001 equivalents (KF:K222:K_2CO_3; 1:4:1);



Integration TLC

Substance	R/F	%Total	Type	Area	%Area
		%		Counts	%
Reg #1	0,157	45,52	DD	1478,750	48,36
Reg #2	0,629	48,61	DD	1579,125	51,64
Sum in ROI				3057,875	
Total area				3248,875	
Area RF				3244,750	
BKG1				15,3941	
Remainder RF				186,88	5,76
Remainder (Tot)				191,00	5,88

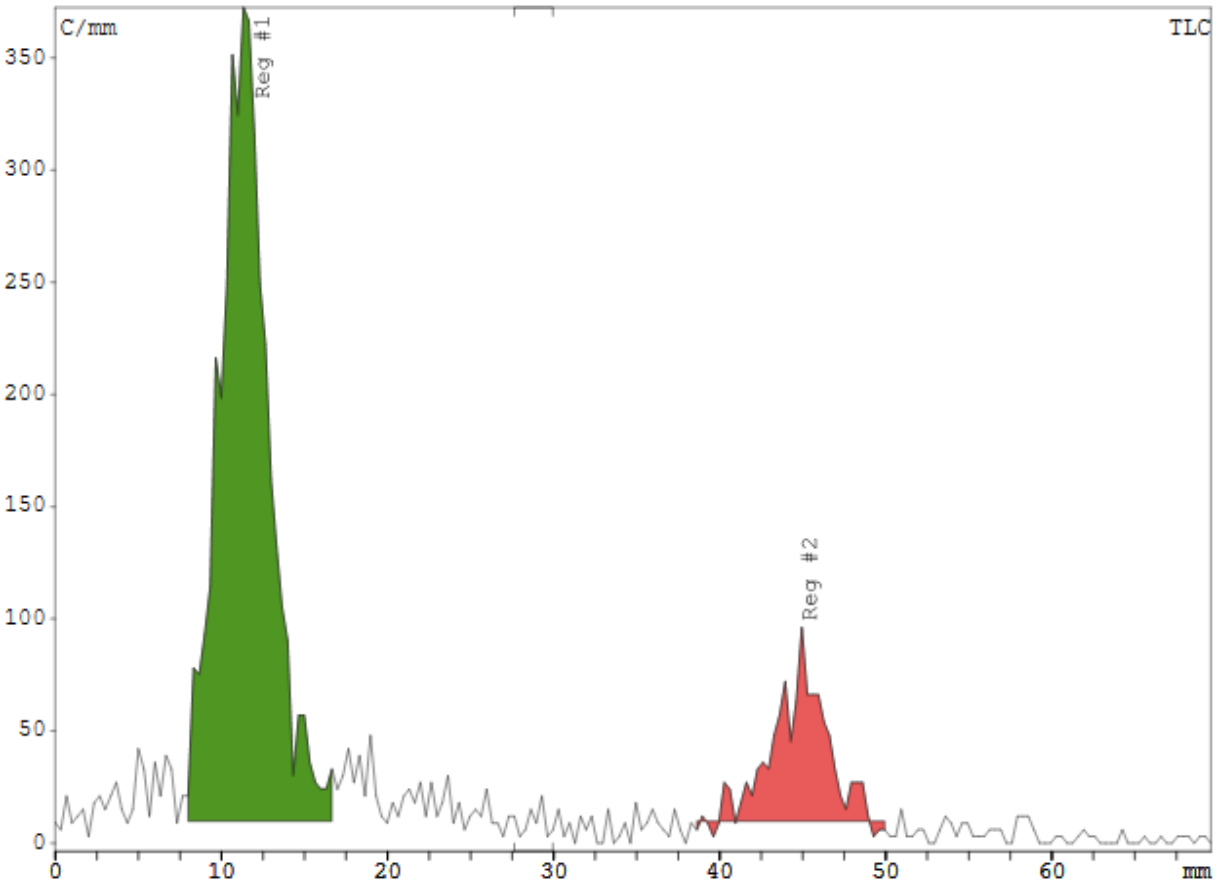
Standard conditions +0.0001 equivalents (KF:K222:K_2CO_3; 1:4:1)



Integration TLC

Substance	R/F	%Total	Type	Area	%Area
		%		Counts	%
Reg #1	0,152	61,45	DD	1877,923	67,45
Reg #2	0,667	29,65	DD	906,308	32,55
Sum in ROI				2784,231	
Total area				3056,231	
Area RF				3054,462	
BKG1				11,3217	
Remainder RF				270,23	8,85
Remainder (Tot)				272,00	8,90

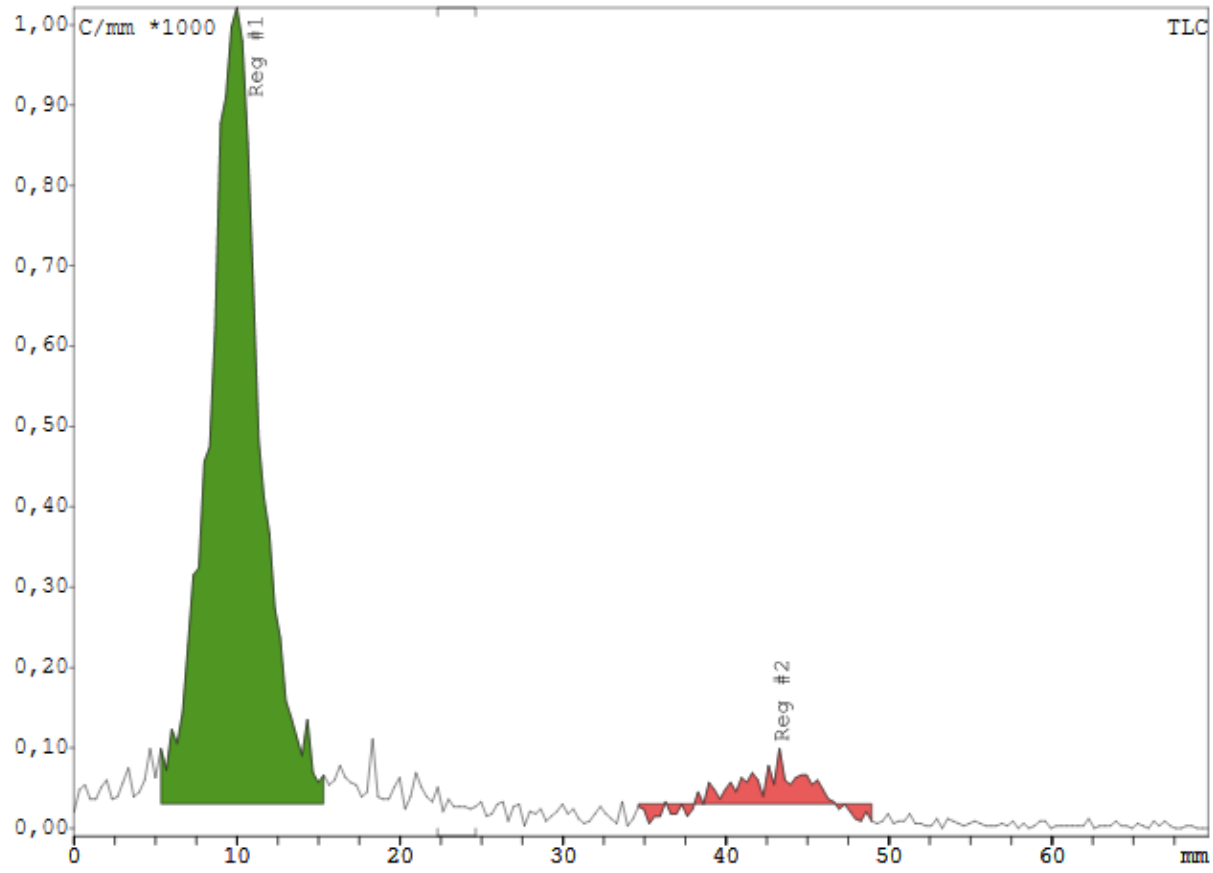
Standard conditions + 0.001 equivalents ($KF:K222:K_2CO_3$; 1:4:1)



Integration TLC

Substance	R/F	%Total	Type	Area	%Area
		%		Counts	%
Reg #1	0,162	80,63	DD	1243,571	82,64
Reg #2	0,648	16,94	DD	261,286	17,36
Sum in ROI				1504,857	
Total area				1542,286	
Area RF				1540,000	
BKG1				9,8694	
Remainder RF				35,14	2,28
Remainder (Tot)				37,43	2,43

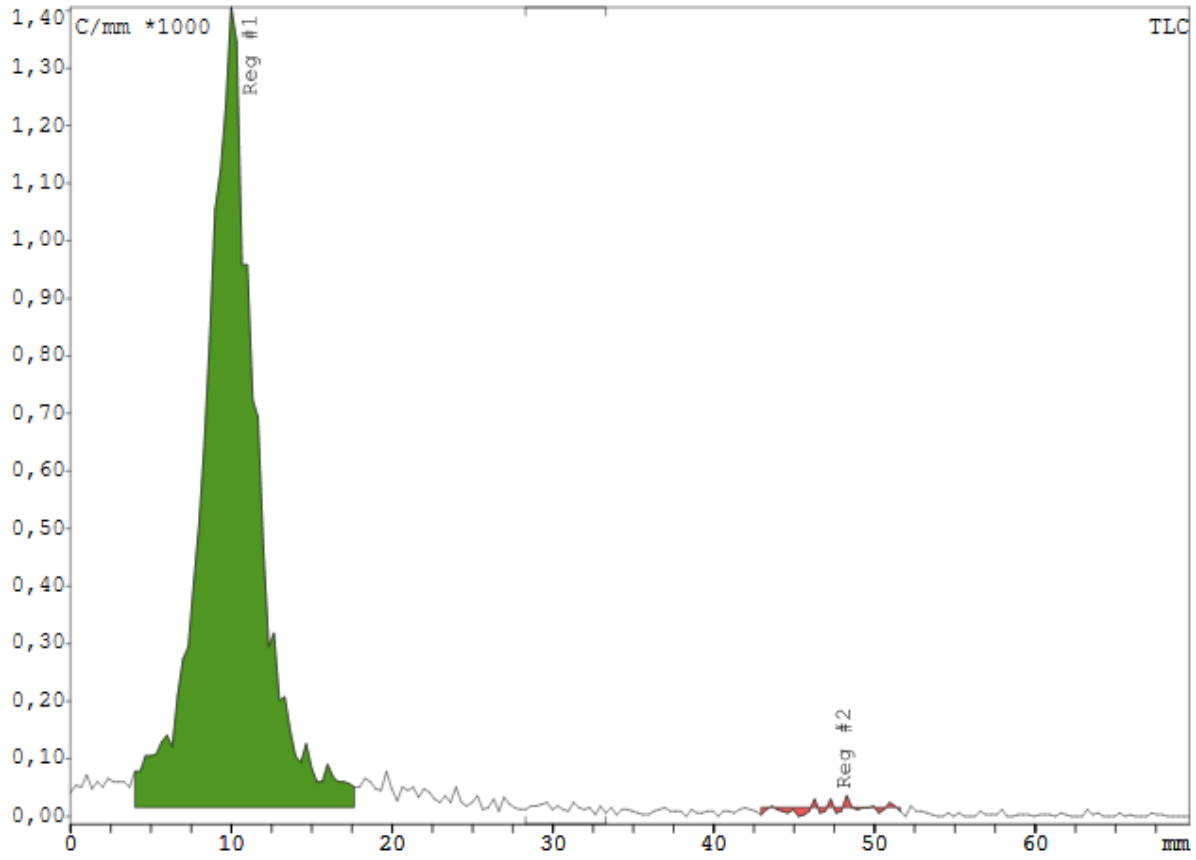
Standard conditions + 0.01 equivalents (KF:K222:K_2CO_3; 1:4:1)



Integration TLC

Substance	R/F	%Total	Type	Area	%Area
		%		Counts	%
Reg #1	0,138	106,53	DD	3629,714	95,96
Reg #2	0,619	4,49	DD	152,857	4,04
Sum in ROI				3782,571	
Total area				3407,143	
Area RF				3397,000	
BKG1				30,4663	
Remainder RF				-385,57	-11,35
Remainder (Tot)				-375,43	-11,02

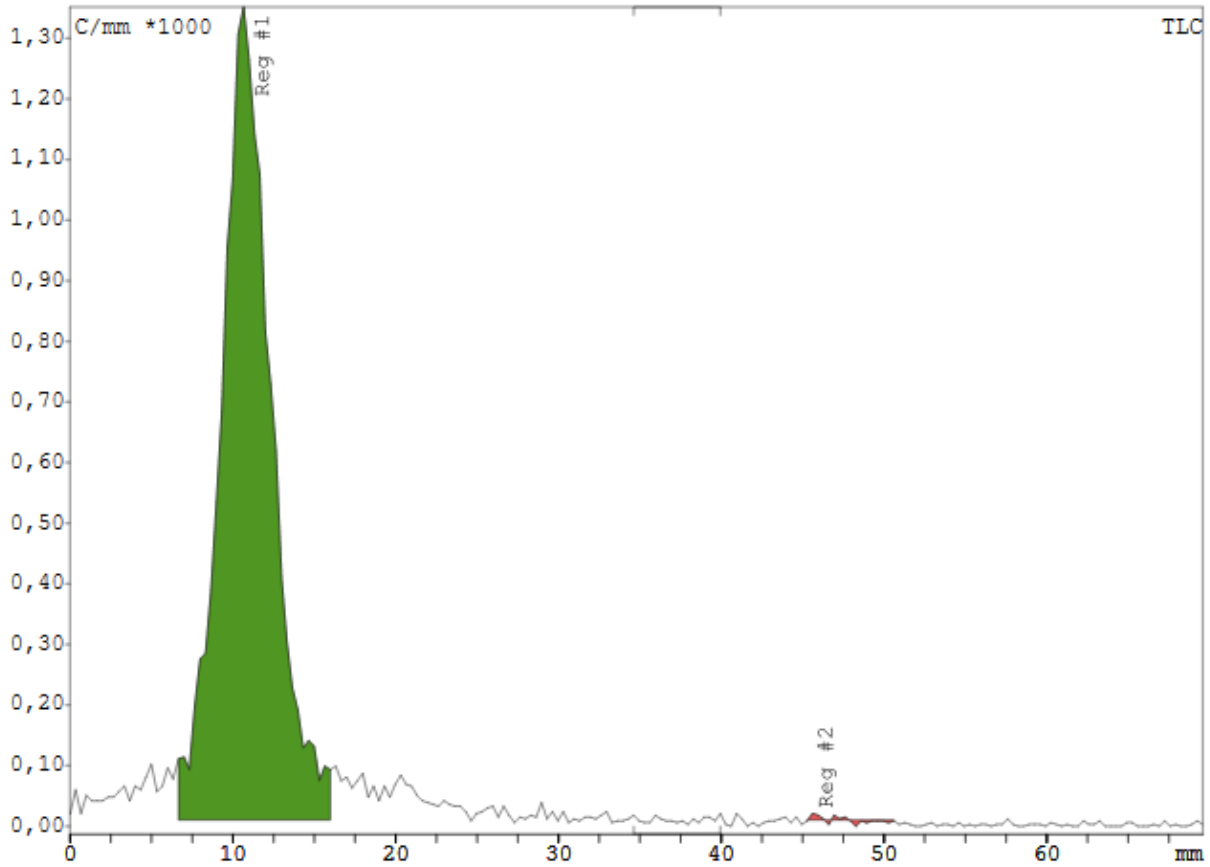
Standard conditions + 0.1 equivalents (KF:K222:K_2CO_3; 1:4:1)



Integration TLC

Substance	R/F	%Total	Type	Area	%Area
		%		Counts	%
Reg #1	0,138	98,51	DD	5128,533	100,36
Reg #2	0,686	-0,35	DD	-18,467	-0,36
Sum in ROI				5110,067	
Total area				5206,133	
Area RF				5201,000	
BKG1				15,4191	
Remainder RF				90,93	1,75
Remainder (Tot)				96,07	1,85

Standard conditions +1 equivalents (KF:K222:K_2CO_3; 1:4:1)

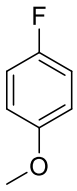


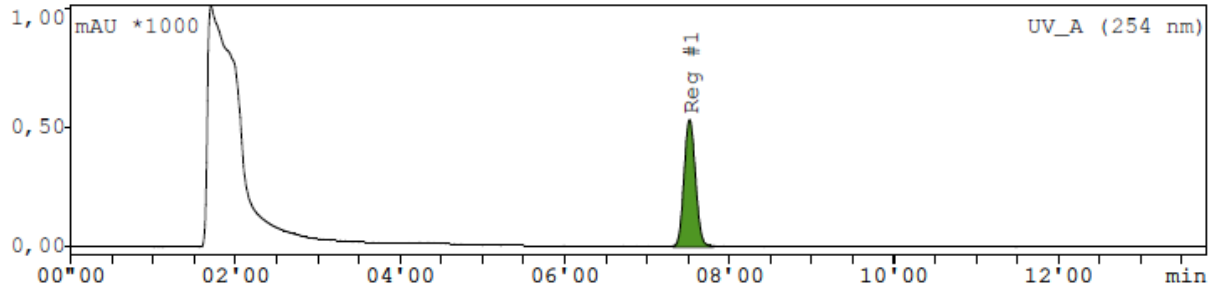
Integration TLC

Substance	R/F	%Total	Type	Area	%Area
		%		Counts	%
Reg #1	0,157	88,15	DD	4808,500	99,98
Reg #2	0,662	0,02	DD	1,000	0,02
Sum in ROI				4809,500	
Total area				5454,625	
Area RF				5454,250	
BKG1				10,1376	
Remainder RF				644,75	11,82
Remainder (Tot)				645,13	11,83

HPLC chromatogram for reference compounds

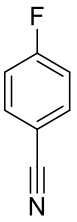
Reference HPLC chromatograms

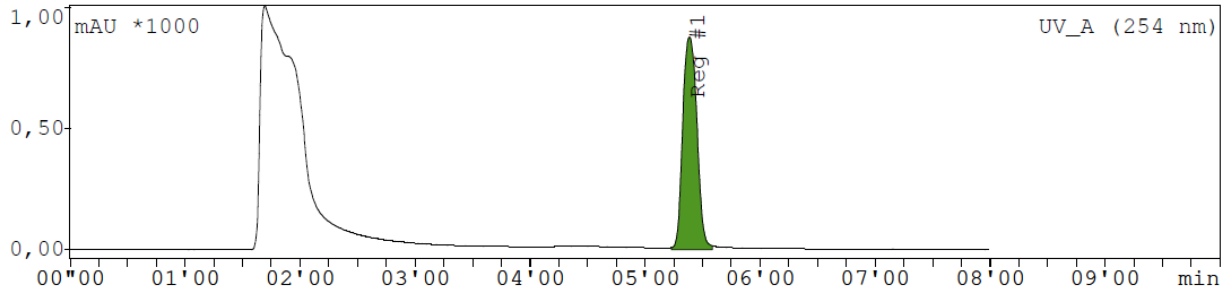




Integration UV_A (254 nm)

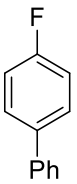
Substance	R/T s	Type	Area mAU*s	%Area %
Reg #1	07'31	DD(M	5077,713	100,00
Sum in ROI			5077,713	100,00

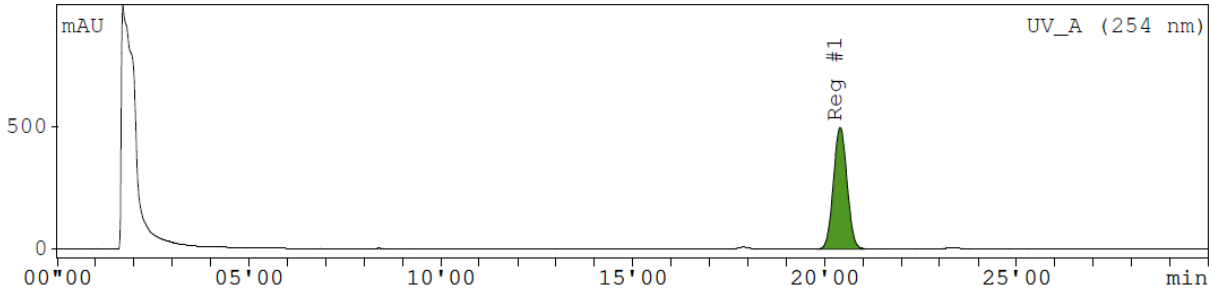




Integration UV_A (254 nm)

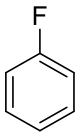
Substance	R/T s	Type	Area mAU*s	%Area %
Reg #1	05'23	DD(M	7544,780	100,00
Sum in ROI			7544,780	100,00

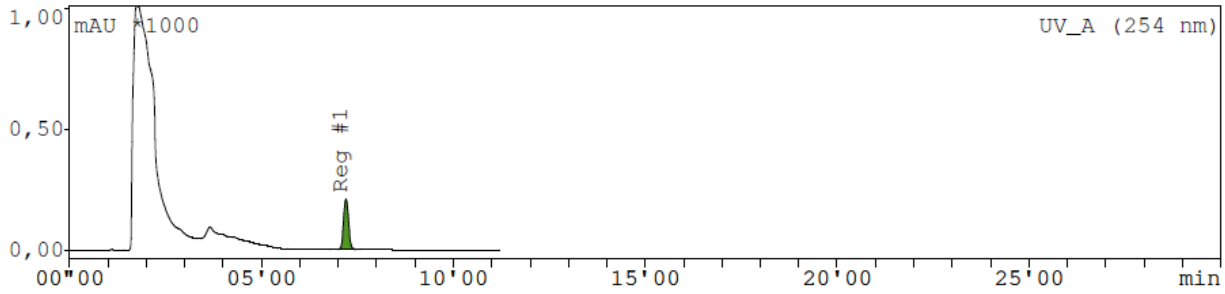




Integration UV_A (254 nm)

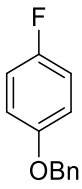
Substance	R/T s	Type	Area mAU*s	%Area %
Reg #1	20'25	DD(M	12255,08	100,00
Sum in ROI			12255,08	100,00

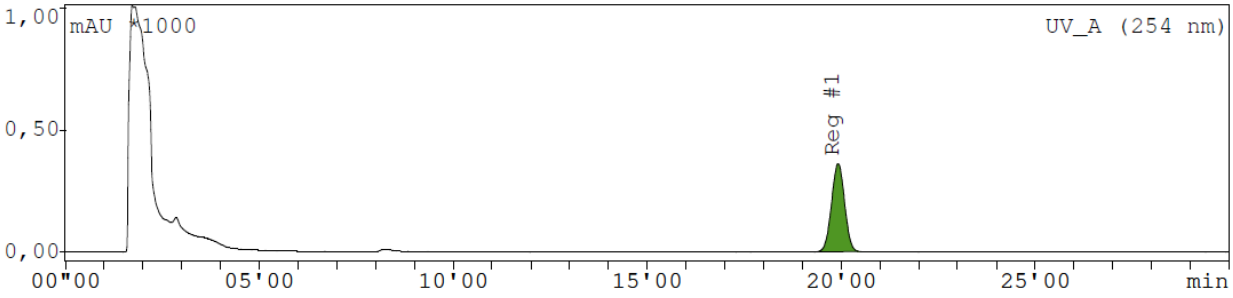




Integration UV_A (254 nm)

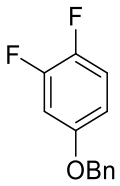
Substance	R/T s	Type	Area mAU*s	%Area %
Reg #1	07'12	BB(M	1829,377	100,00
Sum in ROI			1829,377	100,00

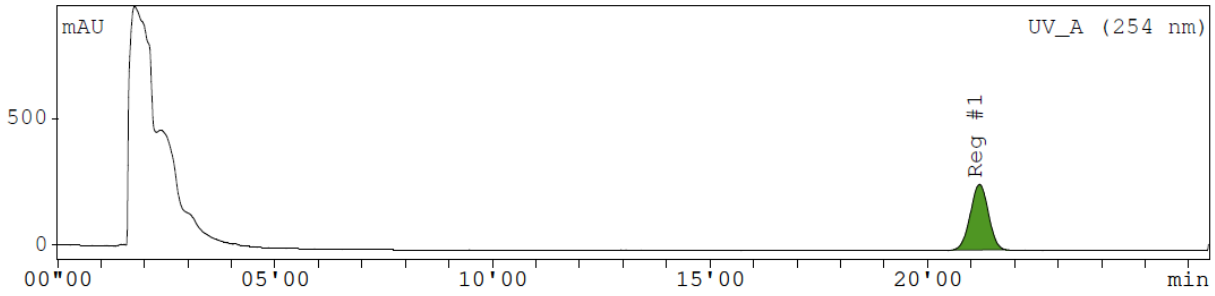




Integration UV_A (254 nm)

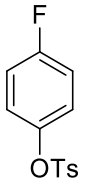
Substance	R/T s	Type	Area mAU*s	%Area %
Reg #1	19'56	BB(M	8329,832	100,00
Sum in ROI			8329,832	100,00

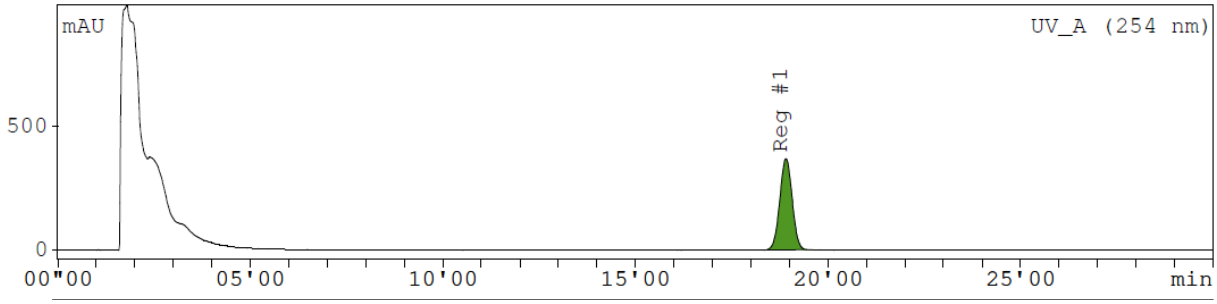




Integration UV_A (254 nm)

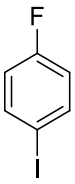
Substance	R/T s	Type	Area mAU*s	%Area %
Reg #1	21'12	BB(M	7519,290	100,00
Sum in ROI			7519,290	100,00

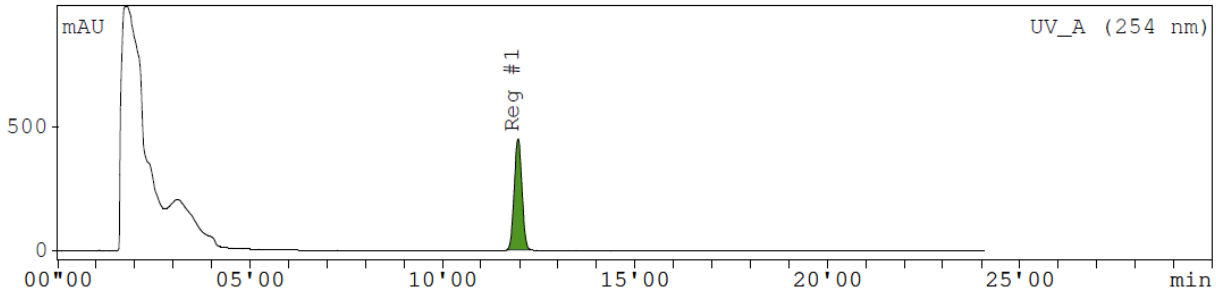




Integration UV_A (254 nm)

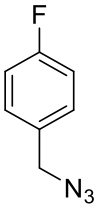
Substance	R/T s	Type	Area mAU*s	%Area %
Reg #1	18'55	BB(M	8182,549	100,00
Sum in ROI			8182,549	100,00

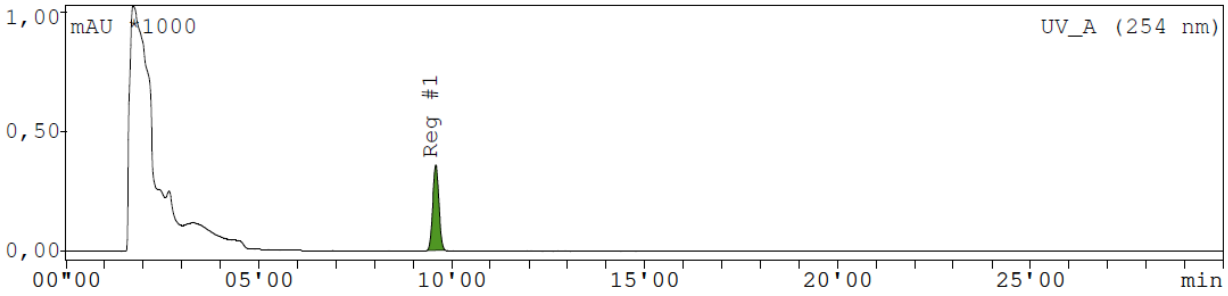




Integration UV_A (254 nm)

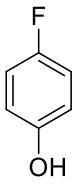
Substance	R/T s	Type	Area mAU*s	%Area %
Reg #1	11'58	BB(M	6147,176	100,00
Sum in ROI			6147,176	100,00

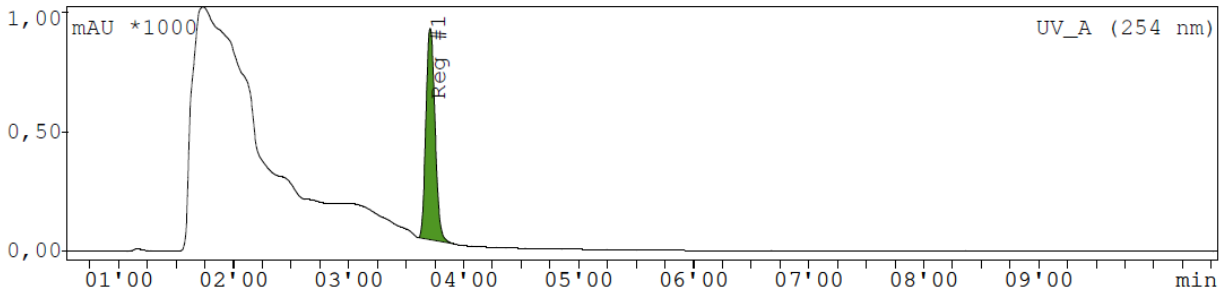




Integration UV_A (254 nm)

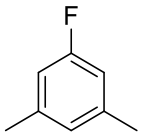
Substance	R/T s	Type	Area mAU*s	%Area %
Reg #1	09'35	BB(M	3878,402	100,00
Sum in ROI			3878,402	100,00

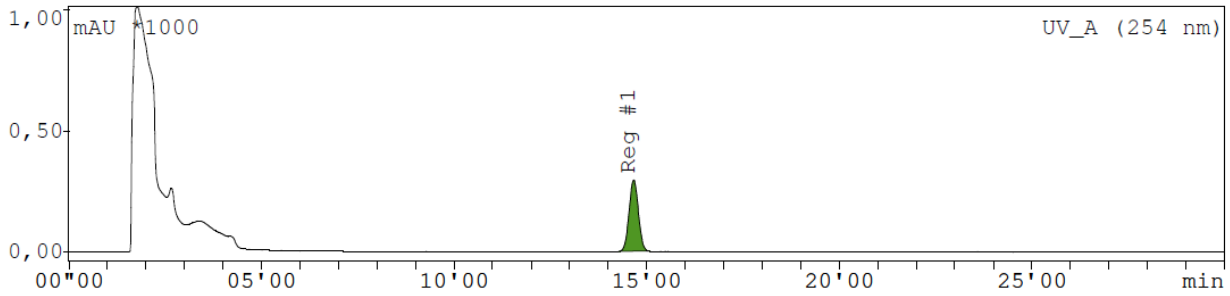




Integration UV_A (254 nm)

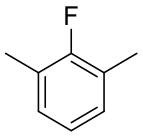
Substance	R/T s	Type	Area mAU*s	%Area %
Reg #1	03'43	BB(M	4814,085	100,00
Sum in ROI			4814,085	100,00

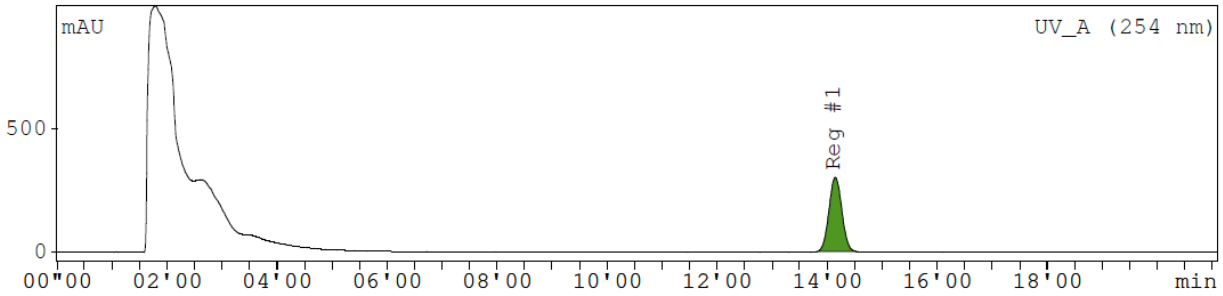




Integration UV_A (254 nm)

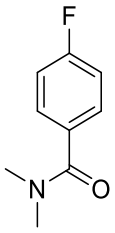
Substance	R/T s	Type	Area mAU*s	%Area %
Reg #1	14'40	BB(M	4914,949	100,00
Sum in ROI			4914,949	100,00

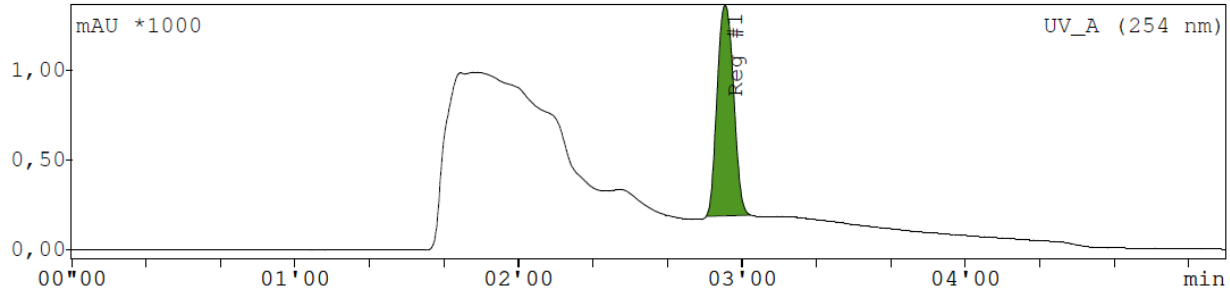




Integration UV_A (254 nm)

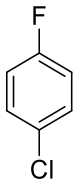
Substance	R/T s	Type	Area mAU*s	%Area %
Reg #1	14'09	BB(M	4780,209	100,00
Sum in ROI			4780,209	100,00

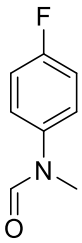


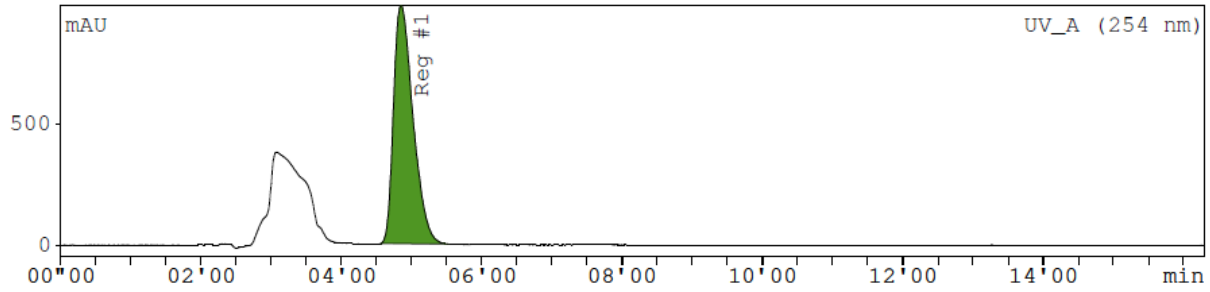


Integration UV_A (254 nm)

Substance	R/T s	Type	Area mAU*s	%Area %
Reg #1	02'56	BB(M	5947,059	100,00
Sum in ROI			5947,059	100,00

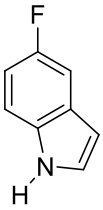


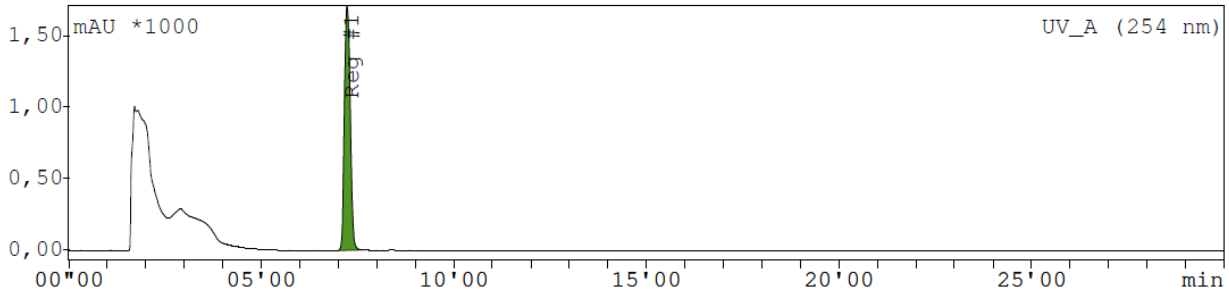




Integration UV_A (254 nm)

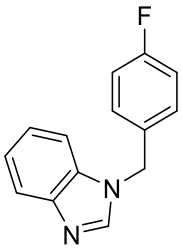
Substance	R/T s	Type	Area mAU*s	%Area %
Reg #1	04'51	BB(M	18822,25	100,00
Sum in ROI			18822,25	100,00

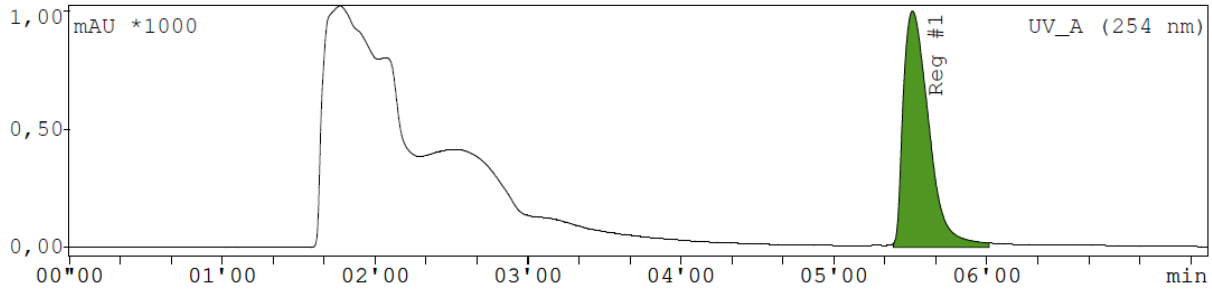




Integration UV_A (254 nm)

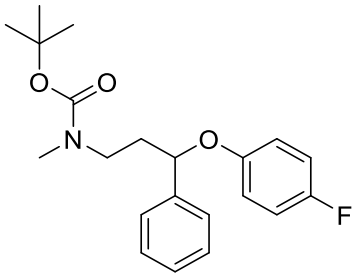
Substance	R/T s	Type	Area mAU*s	%Area %
Reg #1	07'14	BB(M	18043,39	100,00
Sum in ROI			18043,39	100,00

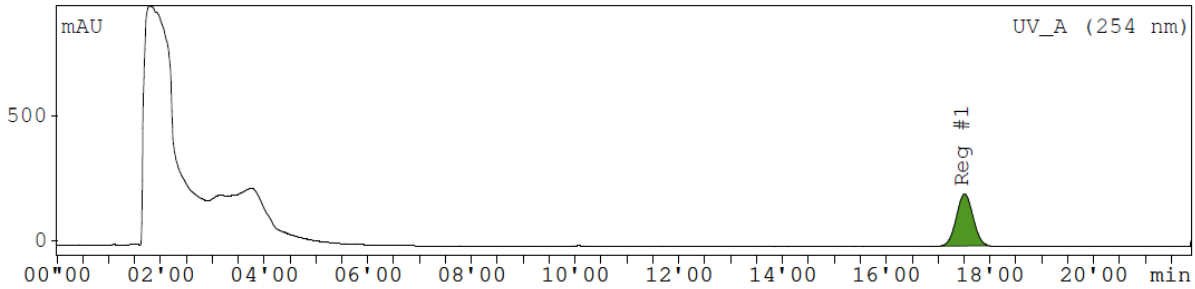




Integration UV_A (254 nm)

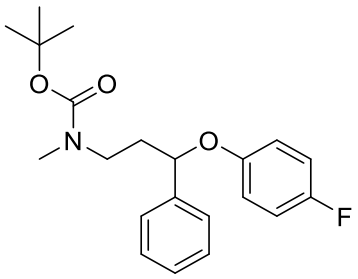
Substance	R/T s	Type	Area mAU*s	%Area %
Reg #1	05'31	DD(M	11663,92	100,00
Sum in ROI			11663,92	100,00

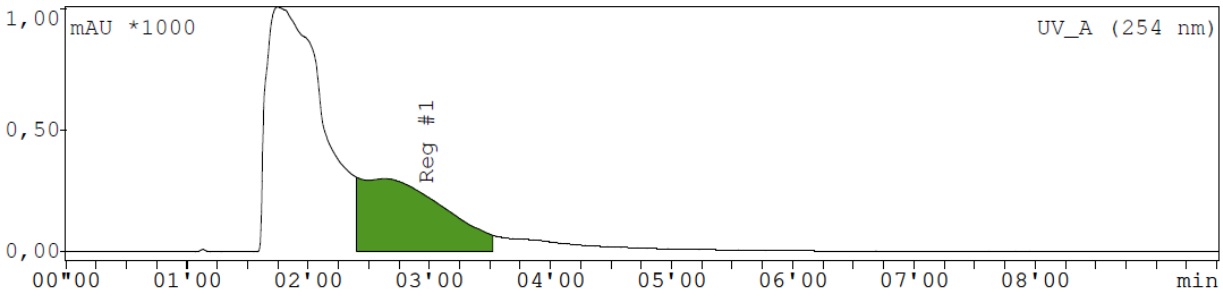




Integration UV_A (254 nm)

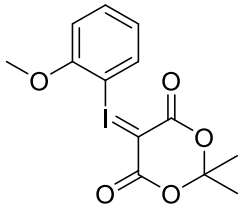
Substance	R/T s	Type	Area mAU*s	%Area %
Reg #1	17'31	BB(M	4651,600	100,00
Sum in ROI			4651,600	100,00

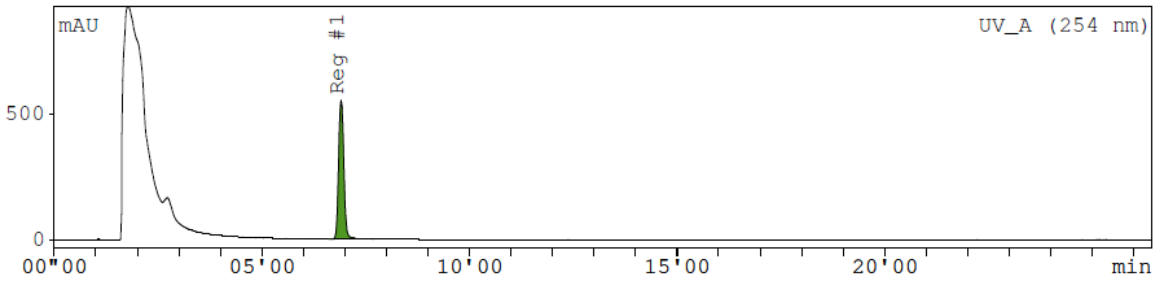




Integration UV_A (254 nm)

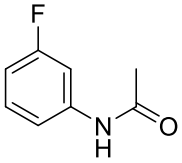
Substance	R/T s	Type	Area mAU*s	%Area %
Reg #1	02'58	DD(M	14415,37	100,00
Sum in ROI			14415,37	100,00

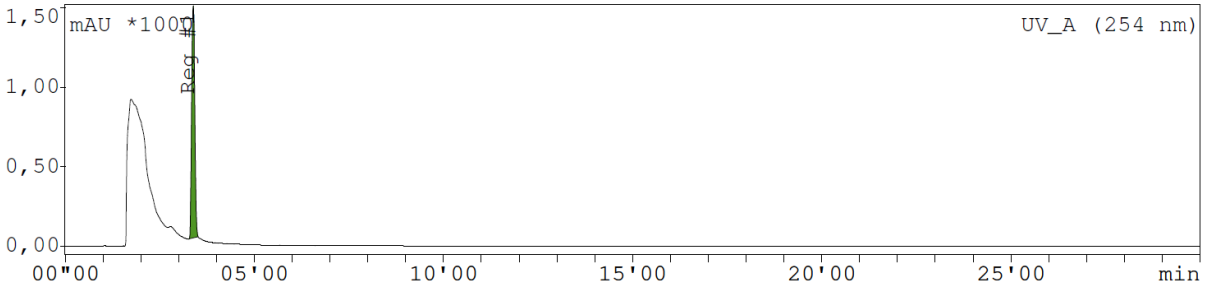




Integration UV_A (254 nm)

Substance	R/T s	Type	Area mAU*s	%Area %
Reg #1	06'55	BB(M	4643,595	100,00
Sum in ROI			4643,595	100,00





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